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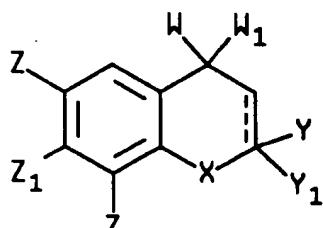
(71) Applicant: AMERICAN CYANAMID COMPANY
One Cyanamid Plaza
Wayne New Jersey 07470 (US)

(72) Inventor: Cary, Gall Ezra
10124 Taylor Court,
Lawrenceville
Mercer, New Jersey 08648 (US)
Inventor: Quinn, Nina Rose
70 Dunkard Church Road,
Stockton
Hunterdon, New Jersey 08559 (US)

(74) Representative: Wächtershäuser, Günter, Prof.
Dr.
Patentanwalt
Tal 29
D-80331 München (DE)

(54) Method for safening herbicides in crops using substituted benzopyran and tetrahydronaphthalene compounds.

(57) There is provided a method for safening herbicides in crop plants by using substituted benzopyran or tetrahydronaphthalene compounds of formula I



(I)

Further provided are compounds of formula II and compositions comprising a herbicide and an antidotally effective amount of a substituted benzopyran or tetrahydronaphthalene compound of formula I.

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BACKGROUND OF THE INVENTION

One of the most common practices for controlling undesirable plant species is the use of herbicides. However, it is known that when certain herbicides are applied in effective amounts they may also damage the crop plants. For example, certain herbicides which are effective against certain annual and perennial grass weeds cannot be used in all crops, especially cereal crops such as corn, sorghum, oat, wheat, barley and rice because the herbicide injures the crops as well as controls the weeds.

It is therefore an object of the present invention to provide a method for protecting crops from injury caused by an herbicide which comprises applying to the crop plant, the seed of the crop, or the soil or water surrounding the crop or crop seed an effective antidotal amount of a substituted benzopyran or tetrahydronaphthalene compound.

It is also an object of the present invention to provide a safened herbicidal composition comprising a herbicide and a substituted benzopyran or tetrahydronaphthalene compound.

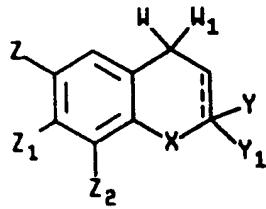
It is a further object of this invention to provide compounds useful as safeners.

These and other objects of the present invention will become more apparent from the detailed description thereof set forth below.

SUMMARY OF THE INVENTION

The present invention relates to a method for protecting crops from injury caused by a herbicidally effective amount of a herbicide by applying to the crop plant, the seed of the crop, or the soil or water surrounding the crop or crop seed an effective antidotal amount of a substituted benzopyran or tetrahydronaphthalene compound of formula I

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wherein

X is O, S(O)_q or CH₂;
q is an integer of 0, 1 or 2;
Z, Z₁ and Z₂ are each independently hydrogen,

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halogen, C₃-C₁₀ alkenyl, C₃-C₁₀ alkynyl, furfuryl, C₁-C₇ alkoxy, C₃-C₁₀ alkenyloxy, Z₃C(O), Z₄S(O)_p, C₁-C₁₀ alkyl optionally substituted with one or more halogen atoms, hydroxy groups, amino groups, thio groups, C₁-C₅ alkylcarbonyl groups or C₁-C₅ alkoxy groups, or

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phenoxy optionally substituted with one or more halogen atoms or C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms;

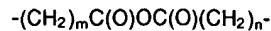
Z₃ is C₁-C₆ alkyl;
Z₄ is C₁-C₆ alkyl;
p is an integer of 0, 1 or 2;

Y and Y₁ are each independently hydrogen,

C₁-C₆ alkyl, halogen, phenyl, C₁-C₆ alkoxy, amino or C₁-C₆ alkylcarbonyl; --- represents a single or double bond with the proviso that when --- represents a double bond then Y₁ is not present;

W and W₁

are each independently (CRR₁)_nA, and when taken together with the carbon atom to which they are attached W and W₁ may form a ring in which WW₁ is represented by the structure:



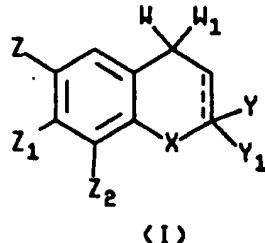
- n is with the proviso that when n is 1 then m is 1;
 m is an integer of 0 or 1;
 5 r is an integer of 1 or 2;
 R is an integer of 0, 1, 2 or 3;
 hydrogen, C₁-C₁₀ alkyl, C₃-C₆ alkenyl, C₃-C₆ alkynyl, C₃-C₆ cycloalkyl or C₁-C₁₀ alkoxy;
 R₁ is hydrogen or C₁-C₁₀ alkyl;
 10 A is C(O)X₁, C(S)OR₂, CR₃(OR₄)₂ or cyano;
 X₁ is OR₅, R₆, NR₇R₈ or SR₉;
 R₂, R₅ and R₉ are each independently hydrogen,
 C₃-C₁₀ alkenyl, C₃-C₁₀ alkynyl, furfuryl,
 C₁-C₁₀ alkyl optionally substituted with one or more halogen atoms, or
 an alkali metal, alkaline earth metal, manganese, copper, zinc, cobalt, silver,
 15 nickel, ammonium or organic ammonium cation;
 R₃ and R₆ are each independently hydrogen or
 C₁-C₁₀ alkyl optionally substituted with one or more halogen atoms;
 R₇ and R₈ are each independently hydrogen, C₃-C₁₀ alkenyl or C₁-C₁₀ alkyl;
 R₄ is C₃-C₁₀ alkenyl, C₃-C₁₀ alkynyl or C₁-C₁₀ alkyl and when taken together R₄ and a
 20 second R₄ may form a ring which R₄R₄ are represented by -(CH₂)₂- or -(CH₂)₃-; and
 the optical isomers thereof.
- The invention also relates to compounds which are useful for safening important agricultural crops against herbicidal injury.
- 25 The invention further relates to a safened herbicidal composition which is effective against weeds, but spares the crop.

DETAILED DESCRIPTION OF THE INVENTION

30 The present invention relates to a method of safening herbicides by applying a chemical safener, a substituted benzopyran or tetrahydronaphthalene compound of formula I, to the seed of the crop, the foliage of the crop or the soil or water surrounding the crop or crop seed.

The safener compounds of the present invention have the following structural formula I

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wherein

- X is O, S(O)_q or CH₂;
- q is an integer of 0, 1 or 2;
- Z, Z₁ and Z₂ are each independently hydrogen,
 50 halogen, C₃-C₁₀ alkenyl, C₃-C₁₀ alkynyl, furfuryl,
 C₁-C₇ alkoxy, C₃-C₁₀ alkenyloxy, Z₃C(O), Z₄S(O)_p,
 C₁-C₁₀ alkyl optionally substituted with one or more halogen atoms, hydroxy groups, amino groups, thio groups, C₁-C₅ alkylcarbonyl groups or C₁-C₅ alkoxy groups, or
 55 phenoxy optionally substituted with one or more halogen atoms or
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms;
- Z₃ is C₁-C₆ alkyl;
- Z₄ is C₁-C₆ alkyl;

	p is Y and Y ₁ are	an integer of 0, 1 or 2; each independently hydrogen, C ₁ -C ₆ alkyl, halogen, phenyl, C ₁ -C ₆ alkoxy, amino or C ₁ -C ₆ alkylcarbonyl;
5	---	represents a single or double bond with the proviso that when --- represents a double bond then Y ₁ is not present;
	W and W ₁	are each independently (CRR ₁)A, and when taken together with the carbon atom to which they are attached W and W ₁ may form a ring in which WW ₁ is represented by the structure:
10		-(CH ₂) _m C(O)OC(O)(CH ₂) _n -
		with the proviso that when n is 1 then m is 1;
	n is	an integer of 0 or 1;
	m is	an integer of 1 or 2;
15	r is	an integer of 0, 1, 2 or 3;
	R is	hydrogen, C ₁ -C ₁₀ alkyl, C ₃ -C ₆ alkenyl, C ₃ -C ₆ alkynyl, C ₃ -C ₆ cycloalkyl or C ₁ -C ₁₀ alkoxy;
	R ₁ is	hydrogen or C ₁ -C ₁₀ alkyl;
	A is	C(O)X ₁ , C(S)OR ₂ , CR ₃ (OR ₄) ₂ or cyano;
20	X ₁ is	OR ₅ , R ₆ , NR ₇ R ₈ or SR ₉ ;
	R ₂ , R ₅ and R ₉ are	each independently hydrogen, C ₃ -C ₁₀ alkenyl, C ₃ -C ₁₀ alkynyl, furfuryl, C ₁ -C ₁₀ alkyl optionally substituted with one or more halogen atoms, or an alkali metal, alkaline earth metal, manganese, copper, zinc, cobalt, silver, nickel, ammonium or organic ammonium cation;
25	R ₃ and R ₆ are	each independently hydrogen or C ₁ -C ₁₀ alkyl optionally substituted with one or more halogen atoms;
	R ₇ and R ₈ are	each independently hydrogen, C ₃ -C ₁₀ alkenyl or C ₁ -C ₁₀ alkyl;
	R ₄ is	C ₃ -C ₁₀ alkenyl, C ₃ -C ₁₀ alkynyl or C ₁ -C ₁₀ alkyl and when taken together R ₄ and a second R ₄ may form a ring which R ₄ R ₄ are represented by -(CH ₂) ₂ - or -(CH ₂) ₃ -; and
30		the optical isomers thereof.
		Preferred safer compounds of the present invention are those wherein
	X is	O, S(O) _q or CH ₂ ;
	q is	an integer of 0, 1 or 2;
35	Z, Z ₁ and Z ₂	are each independently hydrogen, C ₁ -C ₄ alkoxy, F, Cl, Br, phenoxy optionally substituted with one or more halogen atoms or C ₁ -C ₄ alkyl groups optionally substituted with one or more halogen atoms, or C ₁ -C ₄ alkyl optionally substituted with one or more halogen atoms, C ₁ -C ₃ alkoxy groups or hydroxy groups,
40		provided that at least one of Z-Z ₂ is hydrogen and further provided that only one of Z-Z ₂ is phenoxy optionally substituted with one or more halogen atoms or C ₁ -C ₄ alkyl groups optionally substituted with one or more halogen atoms;
	Y and Y ₁ are	each independently hydrogen, C ₁ -C ₃ alkyl, F or Cl, provided that when Y ₁ is F or Cl, then Y is hydrogen;
45	---	represents a single bond;
	W is	CH ₂ A or when taken together with W ₁ , WW ₁ is represented by the structure -CH ₂ C(O)-OC(O)-;
	W ₁ is	A or when taken together with W, W ₁ W is represented by the structure -C(O)OC(O)-CH ₂ -;
50	A is	C(O)X ₁ or CH(OR ₄) ₂ ;
	X ₁ is	OR ₅ or SR ₉ ;
	R ₅ is	hydrogen, C ₁ -C ₆ alkyl, C ₃ -C ₆ alkenyl, C ₃ -C ₆ alkynyl or an alkali metal, alkaline earth metal, manganese, copper, zinc, cobalt, silver, nickel, ammonium or organic ammonium cation;
55	R ₉ is	hydrogen, C ₁ -C ₆ alkyl, C ₃ -C ₆ alkenyl or C ₃ -C ₆ alkynyl;
	R ₄ is	C ₁ -C ₃ alkyl and when taken together R ₄ and a second R ₄ may form a ring in which R ₄ R ₄ are represented by -(CH ₂) ₂ - or -(CH ₂) ₃ -; and

the optical isomers thereof.

More preferred safer compounds of the present invention are those wherein

X is O, S or CH₂;
 Z, Z₁ and Z₂ are each independently hydrogen, C₁-C₄ alkoxy, F, Cl, Br, C₁-C₄ alkyl or
 5 phenoxy optionally substituted with one or more halogen atoms or
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms,
 provided that at least one of Z-Z₂ is hydrogen and further provided that only
 one of Z-Z₂ is phenoxy optionally substituted with one or more halogen atoms or
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms;

10 Y and Y₁ are each independently hydrogen or C₁-C₃ alkyl;

 W is CH₂A or when taken together with W₁, WW₁ is represented by the structure -CH₂C-
 (O)OC(O)-;
 15 W₁ is A or when taken together with W, W₁W is represented by the structure -C(O)OC(O)-
 CH₂-;
 A is C(O)OR₅;
 R₅ is hydrogen, C₁-C₆ alkyl or
 an alkali metal, alkaline earth metal, ammonium or organic ammonium cation;
 and
 20 the optical isomers thereof.

A most preferred group of safer compounds of the present invention are those wherein

X is O;
 Z, Z₁ and Z₂ are each independently hydrogen,
 25 C₁-C₄ alkoxy, F, Cl, Br, C₁-C₄ alkyl or
 phenoxy optionally substituted with one or more halogen atoms or
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms,
 provided that at least one of Z-Z₂ is hydrogen and further provided that only
 one of Z-Z₂ is phenoxy optionally substituted with one or more halogen atoms or
 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms;
 30 Y and Y₁ are each independently hydrogen or C₁-C₃ alkyl;

 W is CH₂A or when taken together with W₁, WW₁ is represented by the structure -CH₂C-
 (O)OC(O)-;
 35 W₁ is A or when taken together with W, W₁W is represented by the structure -C(O)OC(O)-
 CH₂-;
 A is C(O)OR₅;
 R₅ is hydrogen, C₁-C₆ alkyl or
 an alkali metal, alkaline earth metal, ammonium or organic ammonium cation;
 and
 40 the optical isomers thereof.

Another group of most preferred safer compounds of the present invention are those wherein

X is S;
 Z is hydrogen or Cl;
 Z₁, Z₂, Y and Y₁ are hydrogen;
 45 --- represents a single bond;
 W is CH₂C(O)OR₅;
 W₁ is C(O)OR₅; and
 R₅ is hydrogen or
 an alkali metal, alkaline earth metal, ammonium or organic ammonium
 50 cation; and

the optical isomers thereof.

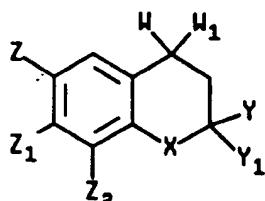
Among the formula I compounds of the present invention which are particularly useful for protecting crops from injury caused by a herbicide are the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;

55 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 4-carboxy-6-[(2-chloro- α,α,α , α -tetrafluoro-p-tolyl)oxy]-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 4-carboxy-3,4-dihydro-6-methoxy-2H-1-benzopyran-4-acetic acid;
 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;

4-carboxy-8-chloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 4-carboxy-6,8-dichloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 4-carboxy-6,7-dichloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 4-carboxy-6-fluoro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 5 7-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 6-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 8-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 4-carboxy-6,8-dibromo-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 4-carboxy-6,8-dimethyl-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 10 2,2',3,3',4',5'-hexahydrospiro[2H-1-benzopyran-4,3'-(2'H)-furan]-2',5'-dione;
 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzopyran-4-acetate, diethyl ester;
 4-carboxy-6-fluoro-3,4-dihydro-2-methyl-2H-1-benzopyran-4-acetic acid as mixture of diastereomers;
 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-acetic acid;
 4-carboxy-3,4-dihydro-2H-1-benzothiopyran-4-acetic acid; and
 15 1-carboxy-1,2,3,4-tetrahydro-1-naphthaleneacetic acid.

The present invention also provides compounds of formula II which are useful as safeners against herbicidal injury in important agronomic crops.

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(II)

30 wherein

X is O or S(O)_q;

q is an integer of 0, 1 or 2;

Z, Z₁ and Z₂ are each independently hydrogen,F, Cl, Br, C₁-C₄ alkoxy,phenoxy optionally substituted with one or more halogen atoms or C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, orC₁-C₄ alkyl optionally substituted with one or more halogen atoms, C₁-C₄ alkoxy groups or hydroxy groups,provided that only one of Z-Z₂ is C₁-C₃ alkoxyalkyl orphenoxy optionally substituted with one or more halogen atoms or C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms;Y and Y₁ are each independently hydrogen, F, Cl or C₁-C₃ alkyl, provided that when Y₂ is F or Cl, then Y₁ is hydrogen;W is CH₂A or when taken together with W₁, WW₁ is represented by the structure -CH₂C-(O)OC(O)-;W₁ is A or when taken together with W, W₁W is represented by the structure -C(O)OC(O)-CH₂-;A is C(O)X₁ or CH(OR₄)₂;X₁ is OR₅ or SR₅;50 R₅ is hydrogen, C₁-C₆ alkyl, C₃-C₆ alkenyl, C₃-C₆ alkynyl or an alkali metal, alkaline earth metal, manganese, copper, zinc, cobalt, silver, nickel, ammonium or organic ammonium cation;R₉ is hydrogen, C₁-C₆ alkyl, C₃-C₆ alkenyl or C₃-C₆ alkynyl;R₄ is C₁-C₆ alkyl and when taken together R₄ and a second R₄ may form a ring in which R₄R₄ are represented by -(CH₂)₂- or -(CH₂)₃-; and

55 the optical isomers thereof;

provided that when Y is hydrogen and Y₁ is hydrogen or C₁-C₃ alkyl, then one of Z, Z₁ or Z₂ is phenoxy optionally substituted with one or more halogen atoms or C₁-C₄ alkyl groups optionally substituted with one

or more halogen atoms.

Preferred saferer compounds of formula II are those wherein

- X is O or S;
- Z is phenoxy optionally substituted with one or more halogen atoms or C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms;
- 5 Z₁ and Z₂ are each independently hydrogen, F, Cl, Br or C₁-C₄ alkyl optionally substituted with one or more halogen atoms, C₁-C₄ alkoxy groups or hydroxy groups;
- Y and Y₁ are each independently hydrogen or C₁-C₃ alkyl;
- W is CH₂C(O)OR₅;
- 10 W₁ is C(O)OR₅; and
- R₅ is hydrogen, C₁-C₆ alkyl or
an alkali metal, alkaline earth metal, ammonium or organic ammonium cation.

More preferred compounds of formula II which are particularly useful as safeners against herbicidal injury in important agronomic crops are those wherein

- 15 X is O;
- Z is phenoxy optionally substituted with one or more halogen atoms or C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms;
- Z₁ and Z₂ are each independently hydrogen, F, Cl or Br;
- Y and Y₁ are each independently hydrogen;
- 20 W is CH₂C(O)OR₅;
- W₁ is C(O)OR₅; and
- R₅ is hydrogen, C₁-C₆ alkyl or
an alkali metal, alkaline earth metal, ammonium or organic ammonium cation.

Alkali metals include: sodium, potassium and lithium, but sodium is generally preferred. Further, the term "organic ammonium" is defined as a group consisting of a positively charged nitrogen atom joined to from one to four aliphatic groups, each containing from one to sixteen carbon atoms. Exemplary of halogen are fluorine, chlorine, bromine and iodine.

Certain formula I compounds may be prepared as shown below in flow diagram I.

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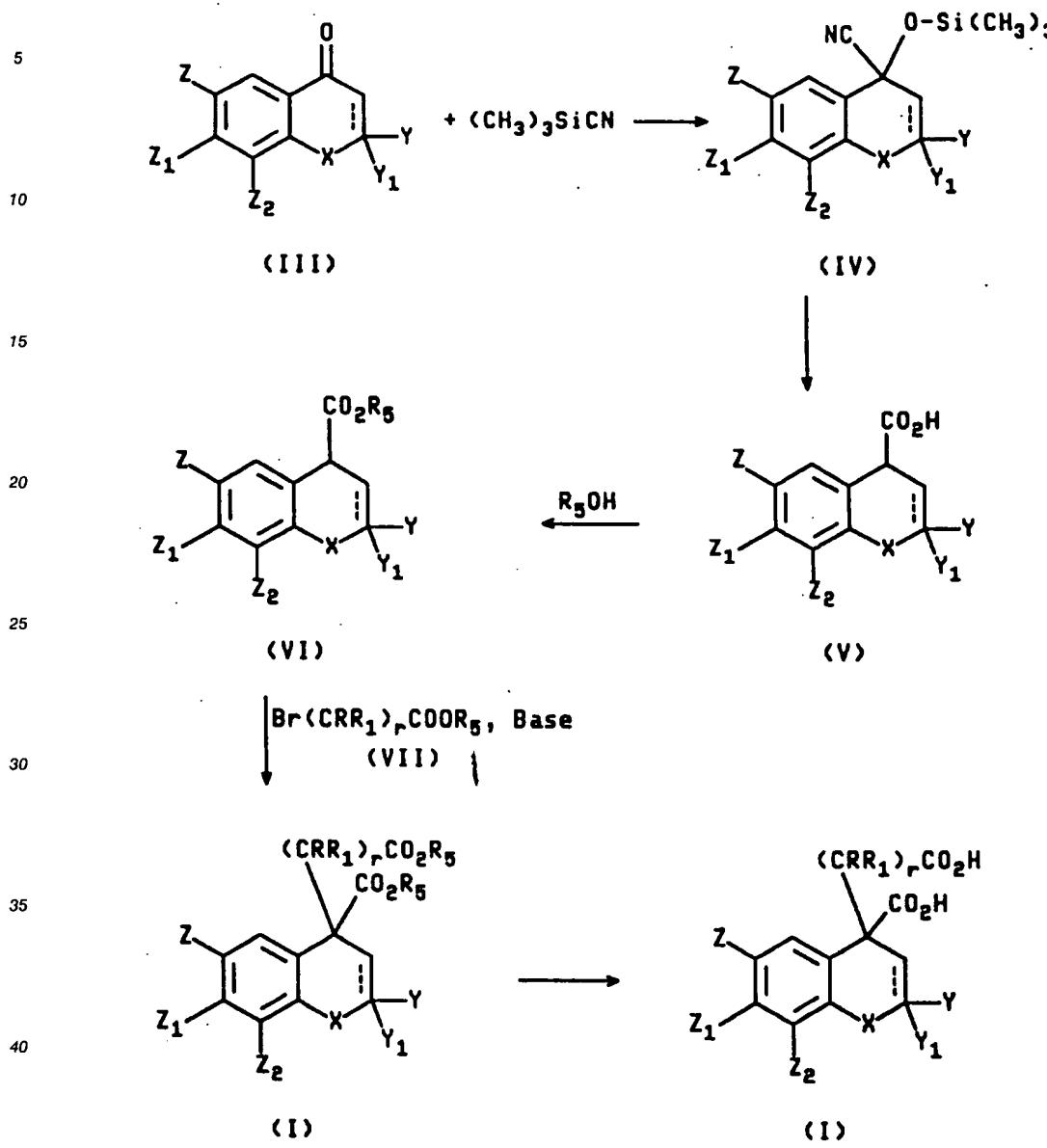
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FLOW DIAGRAM I

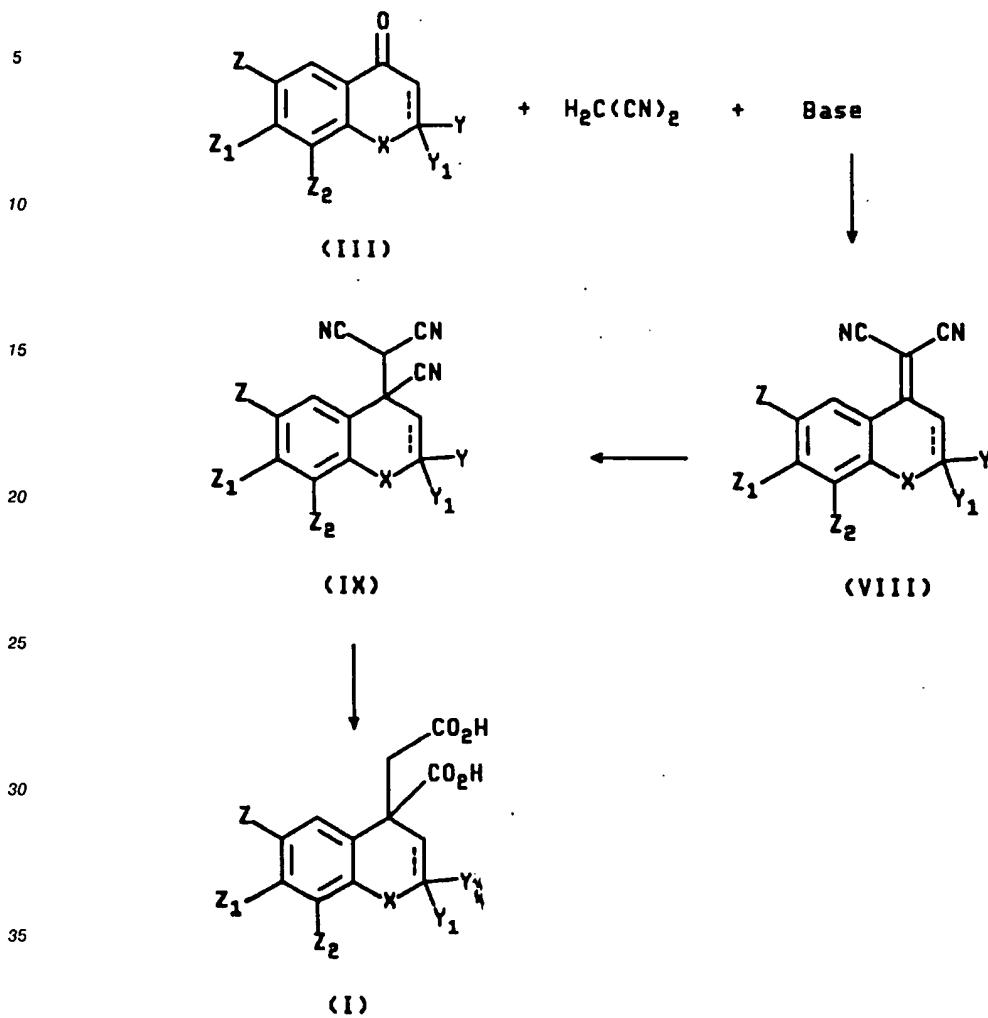
wherein

R_5 is C_3-C_{10} alkenyl, C_3-C_{10} alkynyl, or C_1-C_{10} alkyl optionally substituted with one or more halogen atoms.

The appropriately substituted formula III ketone is reacted with trimethylsilyl cyanide in the presence of a Lewis acid such as zinc iodide to form the formula IV compound. Hydrolysis of the formula IV compound gives the formula V acid which is esterified using standard procedures to obtain the formula VI ester. The formula VI ester is then alkylated with a formula VII bromo ester in the presence of a base such as sodium hydride and a solvent such as 1-methyl-2-pyrrolidinone to give the desired formula I diester. The formula I diester may be hydrolyzed under basic conditions to give the formula I diacid.

Formula I compounds may also be prepared as shown below in flow diagram II.

FLOW DIAGRAM II



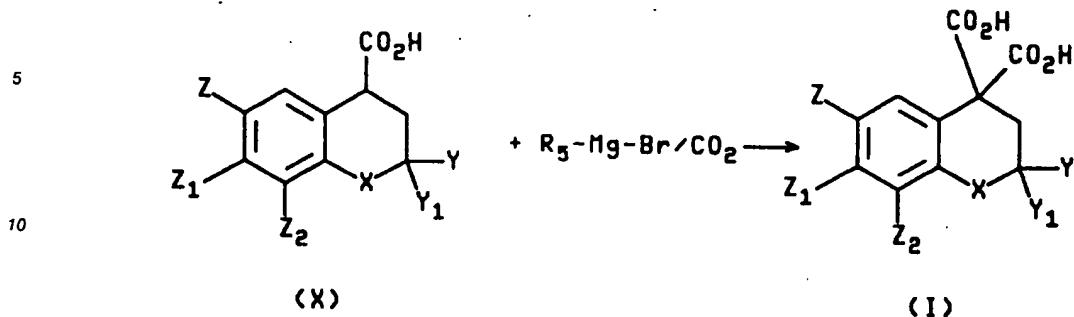
The appropriately substituted formula III ketone is reacted with malononitrile in the presence of a base such as pyridine to form the formula VIII compound. The formula VIII compound is reacted with potassium cyanide in the presence of water to form the formula IX compound which is hydrolyzed with acid or base to obtain the desired formula I diacid.

Other compounds of formula I may be prepared as shown below in flow diagram III.

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FLOW DIAGRAM III

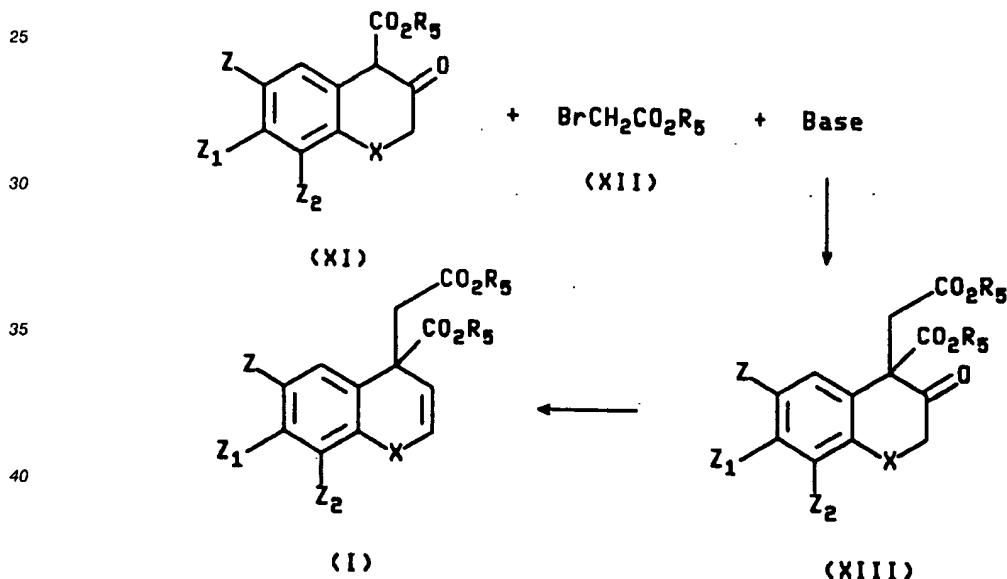


wherein R₅ is C₁-C₁₀ alkyl.

The appropriately substituted formula X carboxylic acid is reacted with a C₁-C₁₀ alkyl-magnesium bromide compound and carbon dioxide to obtain the desired formula I compound.

20 Additional compounds of formula I may be prepared as shown below in flow diagram IV.

FLOW DIAGRAM IV



wherein R₅ is C₁-C₁₀ alkyl.

The appropriately substituted formula XI ketone is reacted with a formula XII bromo ester in the presence of a base to form a formula XIII compound which is reduced to form an intermediate alcohol which is converted to a suitable leaving group such as mesylate and eliminated to give the desired formula I compound.

Surprisingly, it has been found that the compounds of the present invention are especially useful for protecting crops from injury caused by a herbicidally effective amount of a herbicide by applying to the crop plant, the seed of the crop, or the soil or water surrounding the crop or crop seed an effective antidotal amount of a formula I compound.

Herbicides which are suitable for use in the present invention include imidazolinone herbicides such as

5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;

- 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid;
 isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
 methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
 mixture of methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-*p*-toluate and methyl 6-(4-isopropyl-4-
- 5 methyl-5-oxo-2-imidazolin-2-yl)-*m*-toluate; and
 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid;
- sulfonylurea herbicides such as
 methyl o-[{3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido}sulfonyl]benzoate;
 1-[*o*-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-s-triazin-2-yl)urea;
- 10 methyl O-[{[3-(4,6-dimethoxy-2-pyrimidinyl)ureido]-sulfonyl}methyl]benzoate;
 methyl o-[{3-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-ureido]sulfonyl}benzoate;
 1-(4,6-dimethoxy-2-pyrimidinyl)-3-[3-(dimethylcarbamoyl)-2-pyridyl]sulfonylurea;
 ethyl 5-[{3-(4,6-dimethoxy-2-pyrimidinyl)ureido]sulfonyl}-1-methylpyrazole-4-carboxylate;
 15 methyl 3-[{3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-ureido]sulfonyl}-2-thiophenecarboxylate; and
 1-[*o*-(3-chloropropoxy)phenyl]sulfonyl]-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea;
- sulfamoylurea herbicides such as
 1-[*o*-(cyclopropylcarbonyl)phenyl]sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea;
 1-[*o*-acetylphenyl]sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea; and
 1-[*o*-acetylphenyl]sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea;
- 20 oxime herbicides such as
 2-(O-ethyloxime) of 2-butyl-5-[2-(ethylthio)-propyl]-3-hydroxy-2-cyclohexen-1-one;
 sodium salt of methyl 5-butyl-2,2-dimethyl-4,6-dioxocyclohexanecarboxylate, 5-(O-allyloxime);
 2-[O-(3-chloroallyl)oxime of 5-[2-(ethylthio)propyl]-3-hydroxy-2-propionyl-2-cyclohexen-1-one;
 2-(O-ethyloxime) of 2-butyl-3-hydroxy-5-(tetrahydro-2H-thiopyran-3-yl)-2-cyclohexen-1-one; and
- 25 2-(O-ethyloxime) of 3-hydroxy-2-propionyl-5-(2,4,6-trimethylphenyl)-2-cyclohexen-1-one;
 2-(4-aryloxyphenoxy)propionic acid herbicides such as
 methyl 2-{p-[{3-chloro-5-(trifluoromethyl)-2-pyridyl]oxy}phenoxy}propionate;
 methyl 2-[p-(2,4-dichlorophenoxy)phenoxy]propionate;
- 30 butyl 2-{p-[{5-(trifluoromethyl)-2-pyridyl]oxy}phenoxy}propionate;
 butyl 2-{p-[{5-(trifluoromethyl)-2-pyridyl]oxy}phenoxy}propionate, (R)-;
 2-ethoxyethyl 2-{p-[{3-chloro-5-(trifluoromethyl)-2-pyridyl]oxy}phenoxy}propionate;
 1-{2-{p-[{3,5-dichloro-2-pyridyl]oxy}phenoxy}propionyl}isoxazolidine;
 2-[{isopropylideneamino}oxy]ethyl 2-{p-[{6-chloro-2-quinoxalinyl}oxy]phenoxy}propionate, (R)-;
 35 ethyl 2-{p-[{6-chloro-2-quinoxalinyl}oxy]phenoxy}propionate;
 ethyl 2-{p-[{(6-chloro-2-benzoxazolyl)oxy}phenoxy}propionate;
 N-benzoyl-N-(3,4-dichlorophenyl)alanine, ethyl ester;
 2-[{2,4-dichloro-*m*-tolyl]oxy]-2-methylpropionanilide;
- 40 ethyl 2-{p-[{(6-chloro-2-benzoxazolyl)oxy}phenoxy]-propionate;
 N-benzoyl-N-(3-chloro-4-fluorophenyl)alanine, isopropyl ester;
 N-benzoyl-N-(3-chloro-4-fluorophenyl)alanine, methyl ester; and
 methyl *p*,*α*-dichlorohydrocinnamate;
- thiocarbamate herbicides such as
 ethyl dipropylthiocarbamate;
- 45 S-ethyl diisobutylthiocarbamate;
 S-propyl dipropylthiocarbamate;
 S-ethyl hexahydro-1*H*-azepine-1-carbothioate;
 S-(*p*-chlorobenzyl) diethylthiocarbamate; and
 S-benzyl bis(1-methylpropyl)thiocarbamate;
- 50 2-chloroacetanilide herbicides such as
 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-*o*-acetotoluidide;
 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide;
 N-(butoxymethyl)-2-chloro-2'-ethylacetanilide;
 2-chloro-2',6'-diethyl-N-(2-propoxyethyl)acetanilide; and
- 55 2-chloro-N-isopropylacetanilide;
- dinitroaniline herbicides such as
 N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine;
α,*α*-trifluoro-2,6-dinitro-N,N-dipropyl-*p*-toluidine;

3,5-dinitro-N⁴,N⁴-dipropylsulfanilamide;
 N-butyl-N-ethyl- α,α,α -trifluoro-2,6-dinitro-p-toluidine;
 2,6-dinitro-N,N-dipropylcumidine; and
 N-ethyl- α,α,α -trifluoro-N-(2-methylallyl)-2,6-dinitro-p-toluidine; and

- 5 isoxazolyl-2-imidazolidinone herbicides such as
 3-(5-tert-butyl-3-isoxazolyl)-4-hydroxy-1-methyl-2-imidazolidinone; and
 3-(5-tert-butyl-3-isoxazolyl)-1-methyl-2-oxo-4-imidazolidinyl methyl carbamate.

Although, many of these herbicides have been used with success in certain crops, they have been found to be phytotoxic in other crops, especially cereal crops. Surprisingly, it has been found that by 10 applying a substituted benzopyran or tetrahydronaphthalene compound of formula I to the seed of the crop, the foliage of the crop or the soil or water surrounding the crop or crop seed the herbicide is safened.

The present invention also includes a safened herbicidal composition comprising a herbicide and a safener of the invention, a substituted benzopyran or tetrahydronaphthalene compound of formula I.

Safening of crops, especially cereal crops such as corn, sorghum, oat, wheat, barley and rice from the 15 postemergence application of herbicides may be effected by allowing said crop plants to grow until the third to fourth leaf stage then spraying with an aqueous solution of the safener either alone or tank mixed with at least one of the above described herbicides. The tank mix should contain an effective amount of herbicide and an effective amount of safener. Although rates will naturally vary with the particular herbicide and crop, typical rates of application for the safener are about 0.063 kg/ha to 2.0 kg/ha.

20 The present invention may also be practiced by applying the herbicide and/or safener to the soil preemergence. A tank mix of the safener and herbicide may be conveniently prepared and employed or sequential sprayings may be used in accordance with the present method.

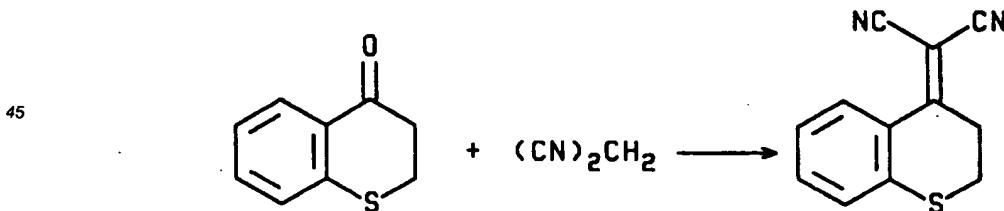
A wide variety of troublesome weed species can also be effectively controlled in the presence of 25 important agronomic crops such as corn, sorghum, oat, wheat, barley and rice by safening the crop plants by any conventional seed treatment techniques or by uniformly coating the seeds with a 5% to 50% wettable powder composition of the safener, planting the coated seed in the usual manner, and spraying the soil with a herbicide or by incorporating the herbicide into the soil before the coated seeds have been planted or by allowing the crop plants from the coated seeds to grow until the third to fourth leaf stage then spraying with a herbicide. Although rates will vary with the particular herbicide and crop, typical rates of 30 application are about 0.10 mg to 4.0 mg of safener per gram of crop seed.

In order to facilitate a further understanding of the invention, the following examples are presented primarily for the purpose of illustrating more specific details thereof. The examples utilize the above reaction schemes and also provide further means for preparing even more compounds of the present invention which are not specifically described above. The invention is not to be deemed limited thereby except as 35 defined in the claims.

EXAMPLE 1

Preparation of 2,3-Dihydro-4H-1-benzothiopyran- $\Delta^{4,\alpha}$ -malononitrile

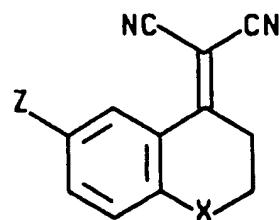
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A mixture of 4-thiochromanone (50.0 g, 0.304 mol) and malononitrile (30.17 g, 0.457 mol) in pyridine is stirred at room temperature for several days, treated with additional malononitrile (30.17 g, 0.457 mol), stirred at room temperature for several days and diluted with a 0.5 N hydrochloric acid/ether mixture. The 55 diluted reaction mixture is filtered to obtain a solid which is dried overnight in a vacuum oven to give the title product as an orange solid (28.5 g, mp 116.5°-118.5°C).

Using essentially the same procedure, but substituting the appropriate starting material for 4-thiochromanone, the following compounds are obtained:



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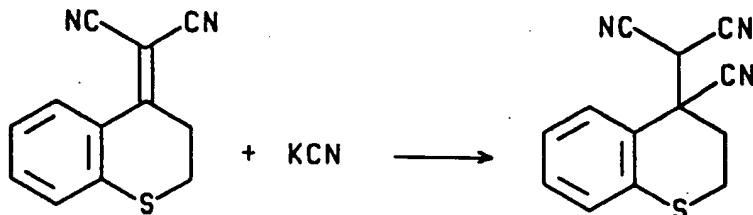
X	Z	mp°C
O	C ₆ H ₅	147 - 149
CH ₂	H	100 - 105

EXAMPLE 2

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Preparation of 4-Cyano-3,4-dihydro-2H-1-benzothiopyran-4-malononitrile

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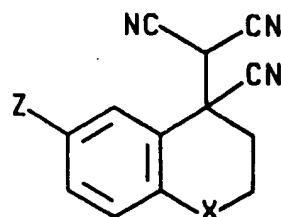


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A mixture of 2,3-dihydro-4H-1-benzothiopyran- $\Delta^{4,\alpha}$ -malononitrile (20.0 g, 0.094 mol) in a 1:1 tetrahydrofuran/ethanol solution is treated dropwise with a solution of potassium cyanide (12.65 g, 0.188 mol) in water over 15 minutes. After stirring for 4 hours, the reaction mixture is added dropwise to a hydrochloric acid/ice mixture to obtain a solid which is extracted with ether. The combined organic extracts are dried over anhydrous MgSO₄ and concentrated in vacuo to give the title product as a pale yellow solid (21.73 g, mp 135.5°-137°C).

Using essentially the same procedure, but substituting the appropriate starting material for 2,3-dihydro-4H-1-benzothiopyran- $\Delta^{4,\alpha}$ -malononitrile, the following compounds are obtained:

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X	Z	mp°C
O	C ₆ H ₅	171 - 173
CH ₂	H	

EXAMPLE 3**Preparation of 4-Carboxy-3,4-dihydro-2H-1-benzothiopyran-4-acetic acid**

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A mixture of 4-cyano-3,4-dihydro-2H-1-benzothiopyran-4-malononitrile (20.5 g, 0.086 mol) in 1:1 acetic acid/hydrochloric acid is heated at reflux for 5 days, cooled to room temperature and filtered to obtain a solid. The solid is washed with water and dried in a vacuum oven to give the title product as a red solid (13.54 g, mp 168°-170°C).

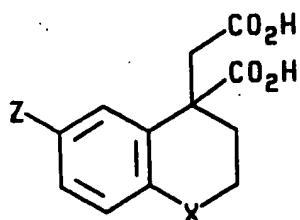
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Using essentially the same procedure, but substituting the appropriate starting material for 4-cyano-3,4-dihydro-2H-1-benzothiopyran-4-malononitrile, the following compounds are obtained:

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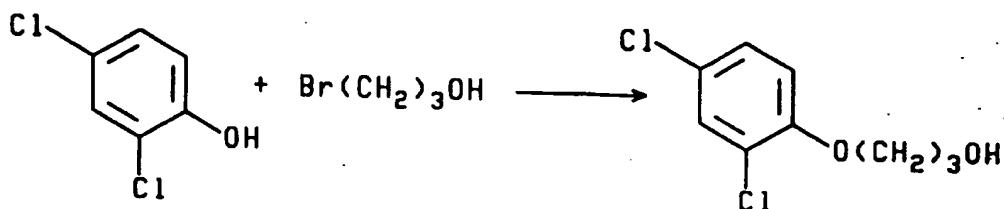
X	Z	mp°C
O	C ₆ H ₅	200 - 202.5
CH ₂	H	146 - 148

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EXAMPLE 4**Preparation of 3-(2,4-Dichlorophenoxy)-1-propanol**

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A solution of 3-bromopropanol (53.86 g, 0.368 mol) in isopropanol is added dropwise to a mixture of 2,4-dichlorophenol (50 g, 0.307 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (70.05 g, 0.406 mol) in isopropanol at reflux. The reaction mixture is heated at reflux for 3 hours and concentrated in vacuo to obtain a residue. The residue is dissolved in methylene chloride and the organic solution is washed

sequentially with 0.5N sodium hydroxide solution, 1M hydrochloric acid and brine, dried over $MgSO_4$ and concentrated in vacuo to obtain an oil which solidifies to give the title product as a white solid (71.9 g, mp 53°-55°C).

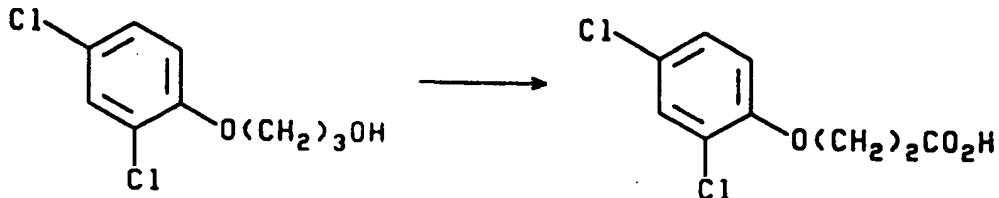
Using essentially the same procedure, but substituting 4-phenylphenol for 2,4-dichlorophenol, 3-(4-phenylphenoxy)-1-propanol is obtained, mp 123°-124°C.

EXAMPLE 5

Preparation of 3-(2,4-Dichlorophenoxy)propionic acid

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Jones reagent (2.3M, 0.283L, 0.650 mol, CrO_3/H_2SO_4) is added to a solution of 3-(2,4-dichlorophenoxy)-1-propanol (71.87 g, 0.325 mol) in acetone while maintaining the temperature of the reaction mixture below 40°C. After the addition is complete, isopropanol is added and the reaction mixture is filtered through diatomaceous earth. The filtrate is concentrated in vacuo to give a blue-green solid which is partitioned between ether and water. The organic phase is separated, washed with brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo to obtain the title product as a yellow solid (69.87 g, mp 93°-95°C).

Using essentially the same procedure, but substituting 3-(4-phenylphenoxy)-1-propanol for 3-(2,4-dichlorophenoxy)-1-propanol, 3-(4-phenylphenoxy)propionic acid is obtained, mp 173°-176°C.

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EXAMPLE 6

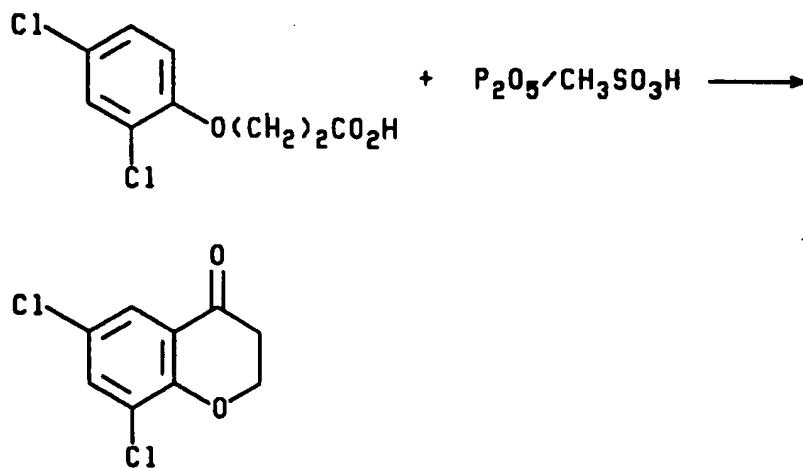
Preparation of 6,8-Dichloro-2,3-dihydro-4H-1-benzopyran-4-one

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3-(2,4-Dichlorophenoxy)propionic acid (52.36 g, 0.223 mol) is added portion-wise to a mixture of phosphorus pentoxide (70.98 g, 0.490 mol) in methanesulfonic acid (Eaton's reagent) under nitrogen. The reaction mixture is stirred at room temperature for 4 hours, poured into water and filtered to obtain a solid. The solid is washed with water and dried in a vacuum oven to give the title product as an off-white solid (45.88 g, mp 86°-87°C).

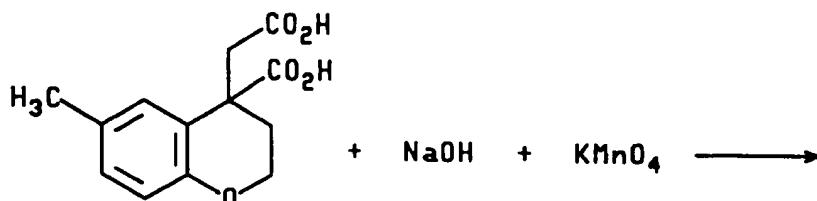
Using essentially the same procedure, but substituting the 3-(4-phenylphenoxy)propionic acid for 3-(2,4-dichlorophenoxy)propionic acid, 6-phenyl-2,3-dihydro-4H-1-benzopyran-4-one is obtained, mp 74°-75°C.

EXAMPLE 7

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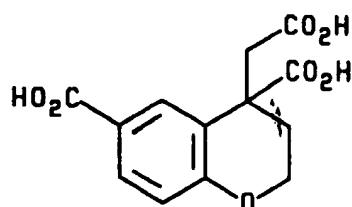
Preparation of 4,6-Dicarboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid

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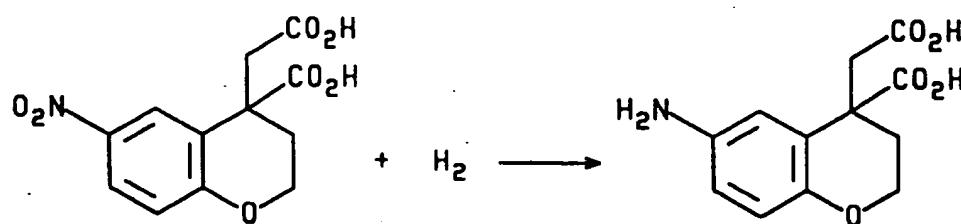
Potassium permanganate (7.52 g, 48 mmol) is added to a mixture of 4-carboxy-3,4-dihydro-6-methyl-2H-benzopyran-4-acetic acid (3.50 g, 14 mmol) and sodium hydroxide (0.84 g, 21 mmol) in water at 50°C. The reaction mixture is stirred at 50° to 60°C overnight and filtered through diatomaceous earth. The filtrate is acidified to pH 1 with hydrochloric acid, washed with an ether/methylene chloride solution and filtered to obtain the title product as a white solid (0.62 g, mp 198°-200°C).

EXAMPLE 8

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Preparation of 6-Amino-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid

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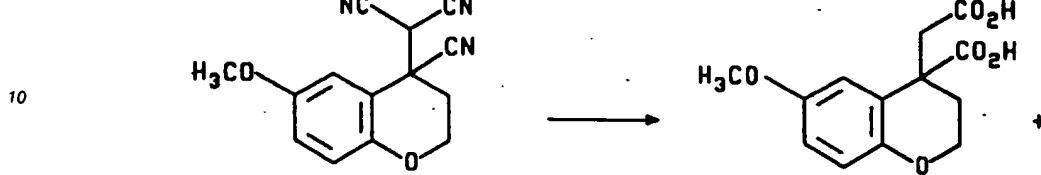


A mixture of 4-carboxy-3,4-dihydro-6-nitro-2H-1-benzopyran-4-acetic acid (4.1 g, 14 mmol), 10% palladium on carbon (1.6 g) and sulfuric acid (1 mL) in ethanol is hydrogenated at 45 psi for 2 hours and filtered through diatomaceous earth. The filtrate is concentrated in vacuo to obtain the title product as a tan solid (2.6 g) which is identified by ¹H and ¹³CNMR spectral analyses.

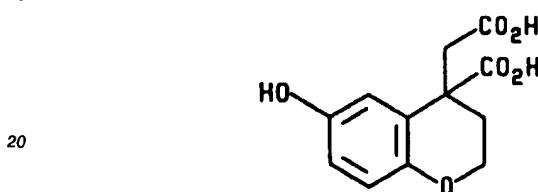
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EXAMPLE 9**Preparation of 4-Carboxy-3,4-dihydro-6-hydroxy-2H-1-benzopyran-4-acetic acid and 4-carboxy-3,4-dihydro-6-methoxy-2H-1-benzopyran-4-aceticacid**

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25 Concentrated hydrochloric acid is added to a mixture of 4-cyano-3,4-dihydro-6-methoxy-2H-1-benzopyran-4-malononitrile (42.76 g, 0.1688 mol) in acetic acid at 30°C. The reaction mixture is heated at reflux for three days, cooled and concentrated *in vacuo* to give a brown solid. The solid is stirred in an ether/water mixture, filtered, washed sequentially with ether and water and dried to obtain 4-carboxy-3,4-dihydro-6-hydroxy-2H-1-benzopyran-4-acetic acid as a gray solid (10.25 g) which is identified by ¹H and ¹³CNMR spectral analyses.

30 The filtrate is concentrated *in vacuo* and partitioned between ether and water. The organic phase is separated and the aqueous phase is extracted with ether. The organic extracts are combined with the organic phase and the organic solution is extracted with 5% sodium hydroxide solution. The 5% sodium hydroxide extracts are acidified with hydrochloric acid, filtered and dried to obtain a solid. The solid is chromatographed using silica gel and a 4:6 acetone/methylene chloride solution to obtain 4-carboxy-3,4-dihydro-6-methoxy-2H-1-benzopyran-4-acetic acid as a brown solid (1.72 g) which is identified by ¹H and ¹³CNMR spectral analyses.

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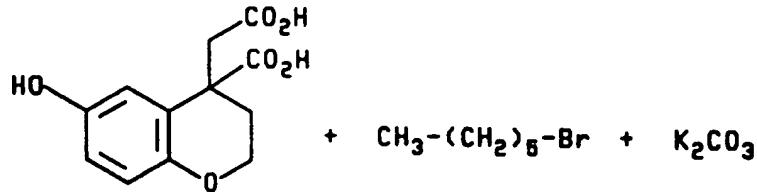
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EXAMPLE 10**Preparation of 4-Carboxy-6-(hexyloxy)-3,4-dihydro-2H-1-benzopyran-4-acetic acid, dihexyl ester**

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25 A mixture of 4-carboxy-3,4-dihydro-6-hydroxy-2H-1-benzopyron-4-acetic acid (0.75 g, 2.97 mmol) and potassium carbonate (1.44 g, 10.40 mmol) in N,N-dimethylformamide is heated to 105°C, cooled to room temperature, treated with n-hexylbromide (0.98 g, 5.94 mmol), heated at 60°C to 90°C overnight, treated with additional n-hexylbromide (0.98 g, 5.94 mmol), heated at 125°C overnight, cooled to room temperature and diluted with water. The aqueous mixture is extracted with ether. The combined organic extracts are washed sequentially with 10% sodium hydroxide solution, water and brine, dried over anhydrous MgSO_4 and concentrated *in vacuo* to obtain a brown syrup. Flash chromatography of the syrup using silica gel and a 1:1 hexanes/methylene chloride solution gives the title product as a pale yellow oil, 1.04 g, which is identified by ^1H and ^{13}C NMR spectral analyses.

30 Using essentially the same procedure, but substituting allyl bromide for n-hexylbromide, 6-(allyloxy)-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid, diallyl ester is obtained as a pale yellow liquid.

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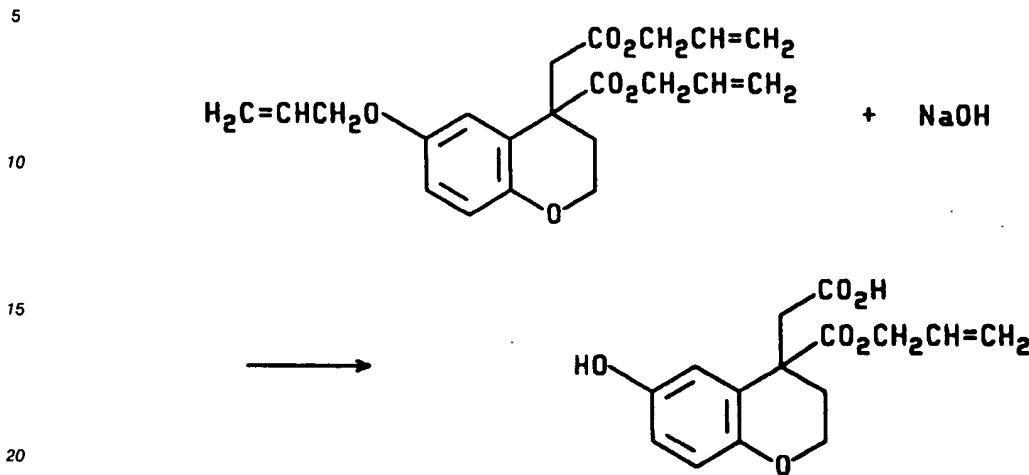
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EXAMPLE 11

Preparation of 3,4-dihydro-6-hydroxy-2H-1-benzopyran-4-acetic acid, 4-carboxylic acid, allyl ester

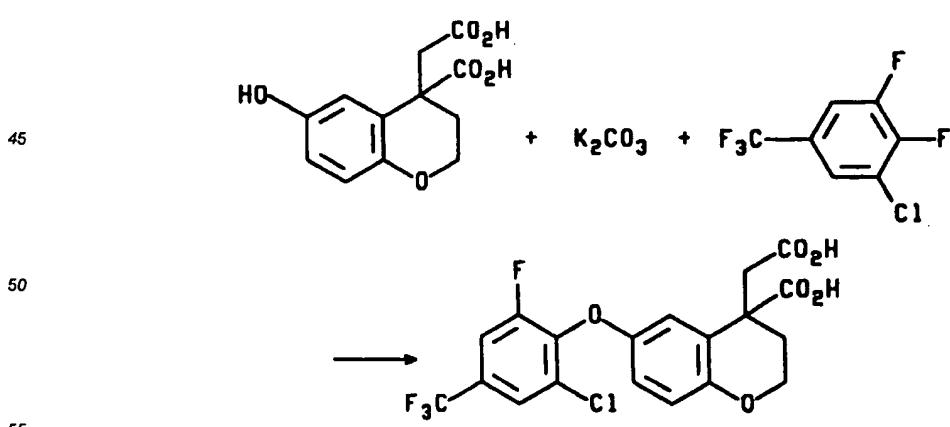


A mixture of 6-(allyloxy)-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid, diallyl ester (0.95 g, 2.55 mmol) and sodium hydroxide (0.26 g, 6.38 mmol) in a water/methanol mixture is heated at reflux overnight, concentrated *in vacuo* and diluted with water. The aqueous mixture is acidified to about pH 1 with 10% hydrochloric acid and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over MgSO₄ and concentrated *in vacuo* to obtain a beige solid. The solid is chromatographed using silica gel and a 2:3 ether/methylene chloride solution to give the title product as a beige solid (0.75 g, mp 147.5°-150°C) which is identified by ¹H and ¹³CNMR spectral analyses.

Using essentially the same procedure, but substituting 4-carboxy-6-(hexyloxy)-3,4-dihydro-2H-1-benzopyran-4-acetic acid, dihexyl ester for 6-(allyloxy)-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid, diallyl ester; 3,4-dihydro-6-hydroxy-2H-1-benzopyran-4-acetic acid, 4-carboxylic acid, hexyl ester is obtained as a solid.

EXAMPLE 12

Preparation of 4-Carboxy-6-[(2-chloro- $\alpha,\alpha,6$ -tetrafluoro-p-tolyl)oxy]-3,4-dihydro-2H-1-benzopyran-4-acetic acid

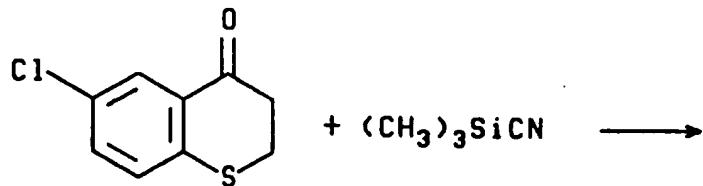


A mixture of 4-carboxy-3,4-dihydro-6-hydroxy-2H-1-benzopyran-4-acetic acid (0.50 g, 1.98 mmol) and potassium carbonate (0.96 g, 6.94 mmol) in N,N-dimethylformamide is heated to 105°C, cooled to 60°C, treated with 3-chloro- $\alpha,\alpha,\alpha,4,5$ -pentafluorotoluene (0.51 g, 2.38 mmol), stirred at room temperature overnight, treated with additional potassium carbonate, (0.48 g) and 3-chloro- $\alpha,\alpha,\alpha,4,5$ -pentafluorotoluene (0.51 g), heated at 100°C for three hours, cooled to room temperature and diluted with water. The aqueous mixture is basified with 10% sodium hydroxide solution and washed with ether. The washed aqueous mixture is acidified to about pH 1 with 10% hydrochloric acid and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over MgSO₄ and concentrated in vacuo to obtain a tan foam. The foam is stirred in carbon tetrachloride at reflux and filtered to obtain the title product as a yellow solid (0.6 g, mp 205°-208°C).

EXAMPLE 13**Preparation of 6-Chloro-3,4-dihydro-4-(trimethylsiloxy)-2H-1-benzothiopyran-4-carbonitrile**

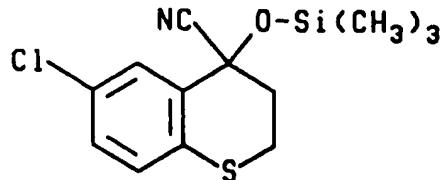
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Under a nitrogen atmosphere, trimethylsilyl cyanide (50.0 g, 0.51 mol) is added to a mixture of 6-chloro-2,3-dihydro-4H-1-benzothiopyran-4-one (25.0 g, 0.126 mol) and anhydrous zinc iodide (1.1 g, 0.0034 mol) over 20 minutes. The reaction mixture is stirred at room temperature for 2 days, diluted with chloroform, washed with sodium hydrogen carbonate solution, dried and concentrated in vacuo to give the title product as a red oil (38.46 g) which is identified by ¹H and ¹³CNMR spectral analyses.

Using essentially the same procedure but substituting 6,8-dichloro-2,3-dihydro-4H-1-benzopyran-4-one for 6-chloro-2,3-dihydro-4H-1-benzothiopyran-4-one, 6,8-dichloro-3,4-dihydro-4-(trimethylsiloxy)-2H-1-benzopyran-4-carbonitrile is obtained as a yellow solid, mp 77°-79°C.

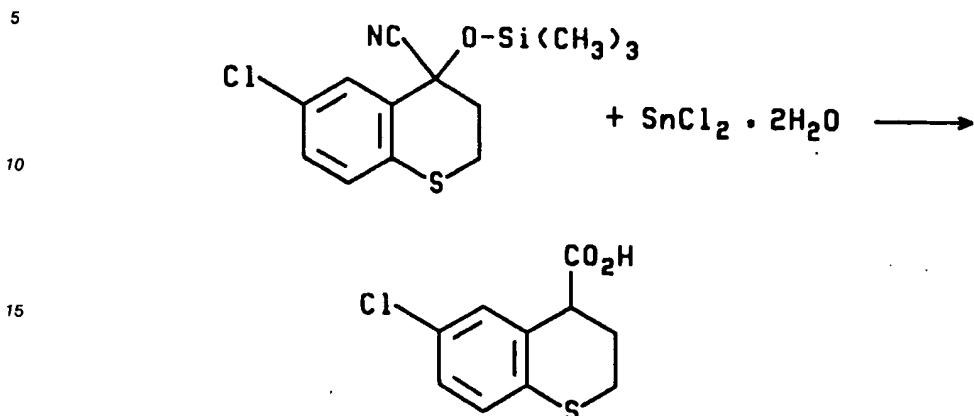
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EXAMPLE 14

Preparation of 6-Chloro-3,4-dihydro-2H-1-benzothiopyran-4-carboxylic acid

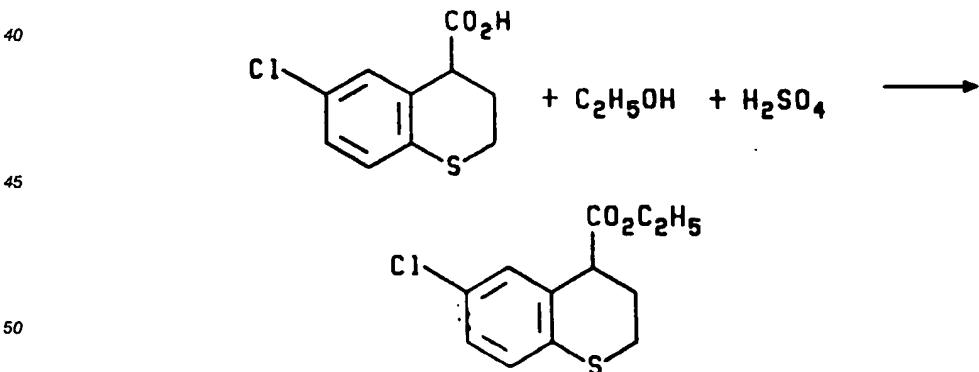


A mixture of tin(II) chloride dihydrate (115.42 g, 0.51 mol) and 6-chloro-3,4-dihydro-4-(trimethylsiloxy)-2H-1-benzothiopyran-4-carbonitrile (37.53 g, 0.126 mol) in 1:1 acetic acid/concentrated hydrochloric acid is heated at reflux under nitrogen for 3 days, cooled to room temperature and diluted with chloroform. The aqueous phase is separated and extracted with chloroform. The organic phase and organic extracts are combined and extracted with 2N sodium hydroxide solution. The combined aqueous extracts are washed with chloroform and acidified to pH 3. The acidic aqueous mixture is extracted with chloroform and the combined organic extracts are dried and concentrated *in vacuo* to obtain a residue. The residue is triturated with an ether/petroleum ether mixture and filtered to give the title product as an off-white solid (12.56 g, mp 139°-150°C).

Using essentially the same procedure but substituting 6,8-dichloro-3,4-dihydro-4-(trimethylsiloxy)-2H-1-benzopyran-4-carbonitrile for 6-chloro-3,4-dihydro-4-(trimethylsiloxy)-2H-1-benzothiopyran-4-carbonitrile, 6,8-dichloro-3,4-dihydro-2H-1-benzopyran-4-carboxylic acid is obtained as a brown oil.

35 EXAMPLE 15

Preparation of Ethyl 6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-carboxylate



55 A mixture of 6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-carboxylic acid (12.56 g, 0.055 mol) and concentrated sulfuric acid (20 mL) in ethanol is heated at reflux for 29 hours, cooled, concentrated *in vacuo* and diluted with a water/methylene chloride mixture. The aqueous phase is separated and extracted with methylene chloride. The organic phase and organic extracts are combined, dried, decolorized with activated

carbon and concentrated in vacuo to give the title product as a pale yellow oil (12.34 g) which is identified by ^1H and $^{13}\text{CNMR}$ spectral analyses.

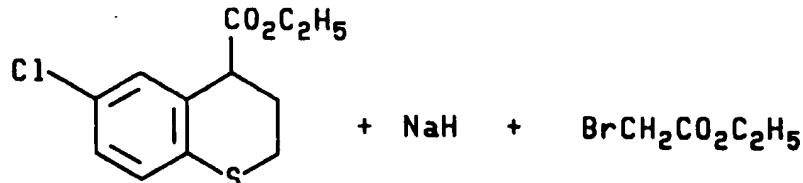
Using essentially the same procedure, but substituting 6,8-dichloro-3,4-dihydro-2H-1-benzopyran-4-carboxylic acid for 6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-carboxylic acid, ethyl 6,8-dichloro-3,4-dihydro-2H-1-benzopyran-4-carboxylate is obtained as a yellow oil.

EXAMPLE 16

Preparation of Diethyl 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-acetate

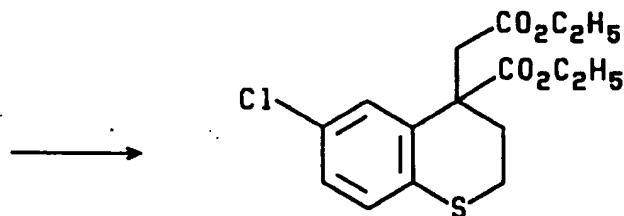
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30 A suspension of sodium hydride (1.43 g, 80% real, 0.048 mol) in 1-methyl-2-pyrrolidinone is treated dropwise with a solution of ethyl 6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-carboxylate (10.64 g, 0.041 mol) in 1-methyl-2-pyrrolidinone over 15 minutes under a nitrogen atmosphere. After stirring for one hour, the reaction mixture is cooled in an ice bath, treated dropwise with ethyl bromoacetate (8.18 g, 0.048 mol), stirred for 5 hours at room temperature, quenched with acetic acid and diluted with a water/methylene chloride mixture. The aqueous phase is separated and extracted with methylene chloride. The organic phase and methylene chloride extracts are combined, washed with water, dried, decolorized with activated carbon and concentrated in vacuo to obtain a residue. The residue is chromatographed using silica gel and a 100:0 to 19:1 hexanes/ethyl acetate solution to give the title product as a yellow oil (10.47 g) which is identified by ^1H and $^{13}\text{CNMR}$ spectral analyses.

35 40 Using essentially the same procedure, but substituting ethyl 6,8-dichloro-3,4-dihydro-2H-1-benzopyran-4-carboxylate for ethyl 6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-carboxylate, diethyl 4-carboxy-6,8-dichloro-3,4-dihydro-2H-1-benzopyran-4-acetate is obtained as a yellow oil.

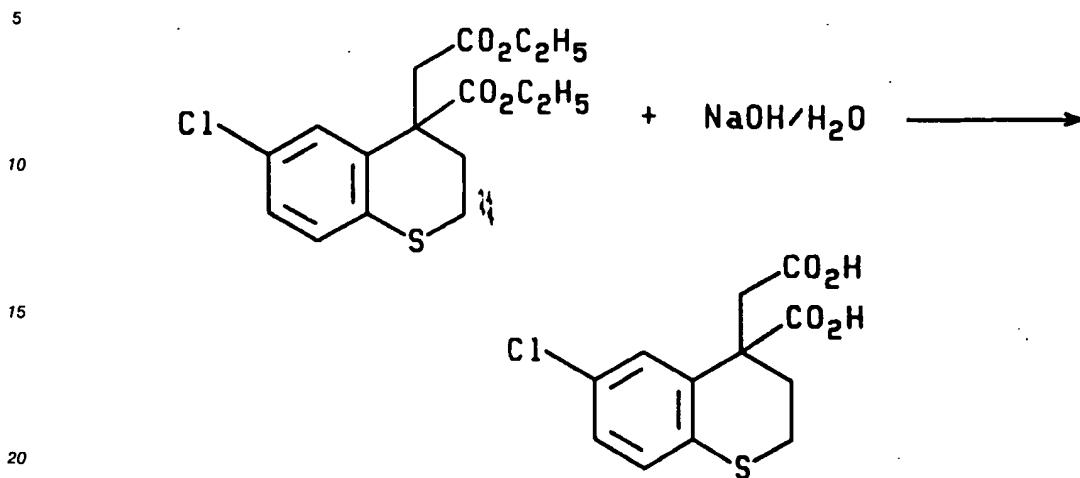
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EXAMPLE 17

Preparation of 4-Carboxy-6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-acetic acid



A solution of diethyl 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-acetate (8.48 g, 0.025 mol) and 1N sodium hydroxide solution (74.2 mL, 0.074 mol) in 1:1 tetrahydrofuran/water is heated at reflux for 48 hours, cooled, concentrated in vacuo, washed with ether, acidified to pH 2.3, stirred in an ice bath for 20 minutes and filtered to obtain a solid. The solid is dried overnight in a vacuum oven to obtain the title product as a white solid (6.81 g, mp 189°-200°C dec.).

30 EXAMPLE 18

Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid as a safener for corn injury from postemergence applications of herbicides

35 Corn plants (Pioneer 3475) in the third leaf stage are sprayed with a formulation of the appropriate
herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diamonium salt of 4-
carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are diluted with water to
provide the equivalent of 0.0015 kg/ha to 0.25 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage
when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray
40 solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl
polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then
placed-on greenhouse benches, watered and cared for in accordance with conventional greenhouse
procedures. From 2-4 weeks after treatment, the tests are terminated and each pot is examined and rated
45 by measuring the height of the-foliage. The test results are averaged and expressed as a percent growth
reduction compared to an untreated check, using the following formula:

$$\% \text{ Growth Reduction} = 100 - \left[\frac{\text{Height of Treated Plants}}{\text{Height of Untreated Plants}} \right] \times 100$$

The results are summarized in Table I wherein

- The results are summarized in Table 1 which is:
 A is the diaminium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 B is methyl o-{{3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido}sulfonyl}benzoate;
 C is 1-[(o-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-S-triazin-2-yl)urea;
 D is 1-[(o-acetylphenyl)sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea;
 E is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid;
 F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;

G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid;
H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
I is 3-{p-[(3,5-dichloro-2-pyridyl)oxy]phenoxy}-2-hydroxybutyronitrile ethyl carbonate;
J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate;
5 K is 3-(5-tert-butyl-3-isoxazolyl)-4-hydroxy-1-methyl-2-imidazolidinone;
L is 2-(O-ethyloxime) of 2-butyryl-5-[2-(ethylthio)-propyl]-3-hydroxy-2-cyclohexen-1-one;
M is ethyl 2-{p-[(6-chloro-2-benzoxazolyl)oxy]phenoxy}propionate;
N is ethyl o-{{(4-chloro-6-methoxy-2-pyrimidinyl)carbamoyl}sulfamoyl}benzoate;
O is 1-[(o-acetylphenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea; and
10 P is 1-[(o-(cyclopropylcarbonyl)phenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea.

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TABLE I

5	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>% Growth Reduction</u>
	B	0.075	23
10	B + A	0.075 + 0.50	2
	B	0.10	29
	B + A	0.10 + 0.50	10
	C	0.0015	67
15	C + A	0.0015 + 0.50	18
	C	0.003	68
	C + A	0.003 + 0.50	15
20	D	0.003	68
	D + A	0.003 + 0.50	60
	E	0.05	28
25	E + A	0.05 + 0.50	6
	E	0.075	71
	E + A	0.075 + 0.50	4
	F	0.05	10
30	F + A	0.05 + 0.50	10
	F	0.10	59
	F + A	0.10 + 0.50	18
35	G	0.012	67
	G + A	0.012 + 0.50	29
	G	0.025	65
40	G + A	0.025 + 0.50	63
	H	0.012	61
	H + A	0.012 + 0.50	41
	H	0.025	66
45	H + A	0.025 + 0.50	63
	I	0.10	41
	I + A	0.10 + 0.50	0
50	I	0.25	63

TABLE I (Continued)

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Treatment	Rate (kg/ha)	Growth Reduction
I + A	0.25 + 0.50	19
J	0.012	67
10 J + A	0.012 + 0.50	63
J	0.025	66
15 J + A	0.025 + 0.50	65
K	0.05	19
K + A	0.05 + 0.50	27
K	0.10	58
20 K + A	0.10 + 0.50	41
L	0.025	38
L + A	0.025 + 0.50	3
L	0.05	68
25 L + A	0.05 + 0.50	39
M	0.012	75
M + A	0.012 + 0.50	75
30 N	0.025	46
N + A	0.025 + 0.50	22
N	0.05	53
35 N + A	0.05 + 0.50	28
O	0.012	6
O + A	0.012 + 0.50	5
O	0.025	39
40 O + A	0.025 + 0.50	9
P	0.012	0
P + A	0.012 + 0.50	-7
45 P	0.025	15
P + A	0.025 + 0.50	-3

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EXAMPLE 19

Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid as a safener for winter barley injury from postemergence applications of herbicides

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Winter barley plants (Volga) approximately 4 to 5 inches tall are sprayed with a formulation of the appropriate herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are

diluted with water to provide the equivalent of 0.012 kg/ha to 0.50 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp.

- 5 Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 2 to 4 weeks after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table II wherein

- 10 A is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
- B is methyl o-{[3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido}sulfonylbenzoate;
- C is 1-[(o-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-S-triazin-2-yl)urea;
- D is 1-[(o-acetylphenyl)sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea;
- E is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid;
- F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
- G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid;
- H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
- I is 3-{p-[3,5-dichloro-2-pyridyl]oxy}phenoxy]-2-hydroxybutyronitrile ethyl carbonate;
- J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate;
- L is 2-(O-ethyloxime) of 2-butyryl-5-[2-(ethylthio)-propyl]-3-hydroxy-2-cyclohexen-1-one;
- M is ethyl 2-{p-[(6-chloro-2-benzoxazolyl)oxy]phenoxy}propionate;
- N is ethyl o-{{[4-chloro-6-methoxy-2-pyrimidinyl]carbamoyl}sulfamoyl}benzoate;
- O is 1-[(o-acetylphenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea;
- P is 1-{{[o-(cyclopropylcarbonyl)phenyl}sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea; and
- 25 Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

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TABLE II

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	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
	B	0.075	69
10	B + A	0.075 + 0.50	69
	B	0.10	71
	B + A	0.10 + 0.50	69
	C	0.05	16
15	C + A	0.05 + 0.50	22
	C	0.10	30
	C + A	0.10 + 0.50	27
20	D	0.025	55
	D + A	0.025 + 0.50	48
	D	0.05	56
25	D + A	0.05 + 0.50	59
	E	0.05	65
	E + A	0.05 + 0.50	59
	E	0.075	68
30	E + A	0.075 + 0.50	67
	F	0.05	22
	F + A	0.05 + 0.50	17
35	F	0.10	32
	F + A	0.10 + 0.50	35
	G	0.012	67
40	G + A	0.012 + 0.50	62
	G	0.025	69
	G + A	0.025 + 0.50	66
	H	0.012	54
45	H + A	0.012 + 0.50	50
	H	0.025	68
	H + A	0.025 + 0.50	67
50	I	0.25	-14

TABLE II (Continued)

5	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
	I + A	0.25 + 0.50	-17
	I	0.50	-14
10	I + A	0.50+ 0.50	-19
	J	0.012	46
	J + A	0.012 + 0.50	19
15	J	0.025	56
	J + A	0.025 + 0.50	55
	L	0.10	13
20	L + A	0.10 + 0.50	11
	L	0.25	30
	L + A	0.25 + 0.50	31
	M	0.025	26
25	M + A	0.025 + 0.50	2
	M	0.05	24
	M + A	0.05 + 0.50	16
30	N	0.025	56
	N + A	0.025 + 0.50	58
	N	0.05	67
35	N + A	0.05 + 0.50	62
	O	0.25	12
	O + A	0.25 + 0.50	11
	O	0.50	29
40	O + A	0.50 + 0.50	15
	P	0.012	-7
	P + A	0.012 + 0.50	-8
45	P	0.025	1
	P + A	0.025 + 0.50	-11
	Q	0.025	31

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TABLE II (Continued)

5	Treatment	Rate (kg/ha)	Growth Reduction
	Q + A	0.025 + 0.50	18
	Q	0.05	29
10	Q + A	0.05 + 0.50	18

EXAMPLE 20

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Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-aceticacid as a safener for sorghum injury from postemergence applications of herbicides

Sorghum plants (NC 271) approximately 4 to 5 inches tall are sprayed with a formulation of the appropriate herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are diluted with water to provide the equivalent of 0.0015 kg/ha to 0.25 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 2 to 4 weeks after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

30 The results are summarized in Table III wherein

- A is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
- B is methyl o-{{3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido}sulfonyl}benzoate;
- C is 1-[(o-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-S-triazin-2-yl)urea;
- D is 1-[(o-acetylphenyl)sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea;
- 35 E is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid;
- F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
- G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinoliniccarboxylic acid;
- H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
- I is 3-{p-[(3,5-dichloro-2-pyridyl)oxy]phenoxy}-2-hydroxybutyronitrile ethyl carbonate;
- 40 J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate;
- K is 3-(5-tert-butyl-3-isoxazolyl)-4-hydroxy-1-methyl-2-imidazolidinone;
- L is 2-(O-ethyloxime) of 2-butyryl-5-[2-(ethylthio)-propyl]-3-hydroxy-2-cyclohexen-1-one;
- M is ethyl 2-{p-[(6-chloro-2-benzoxazolyl)oxy]phenoxy}propionate;
- N is ethyl o-{{[(4-chloro-6-methoxy-2-pyrimidinyl)carbamoyl]sulfamoyl}benzoate};
- 45 O is 1-[(o-acetylphenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea;
- P is 1-{{[o-(cyclopropylcarbonyl)phenyl]sulfamoyl}-3-(4,6-dimethoxy-2-pyrimidinyl)urea; and
- Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

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TABLE III

5	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>\$ Growth Reduction</u>
	B	0.0015	17
10	B + A	0.0015 + 0.50	28
	B	0.003	38
	B + A	0.003 + 0.50	40
	C	0.0015	31
15	C + A	0.0015 + 0.50	11
	C	0.003	34
	C + A	0.003 + 0.50	14
20	D	0.006	31
	D + A	0.006 + 0.50	17
	D	0.012	36
25	D + A	0.012 + 0.50	21
	E	0.025	75
	E + A	0.025 + 0.50	78
	E	0.05	78
30	E + A	0.05 + 0.50	80
	F	0.006	14
	F + A	0.006 + 0.50	4
35	F	0.012	34
	F + A	0.012 + 0.50	23
	G	0.012	35
40	G + A	0.012 + 0.50	24
	G	0.025	36
	G + A	0.025 + 0.50	27
	H	0.012	46
45	H + A	0.012 + 0.50	34

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TABLE III (Continued)

5	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
	H	0.025	70
10	H + A	0.025 + 0.50	75
	I	0.10	3
	I + A	0.10 + 0.50	0
	I	0.25	47
15	I + A	0.25 + 0.50	37
	J	0.012	60
	J + A	0.012 + 0.50	64
20	J	0.025	59
	J + A	0.025 + 0.50	62
	K	0.05	9
25	K + A	0.05 + 0.50	4
	K	0.10	15
	K + A	0.10 + 0.50	29
	L	0.025	13
30	L + A	0.025 + 0.50	12
	L	0.05	54
	L + A	0.05 + 0.50	28
35	M	0.006	63
	M + A	0.006 + 0.50	46
	M	0.012	54
40	M + A	0.012 + 0.50	62
	N	0.025	78
	N + A	0.025 + 0.50	77
	N	0.05	78
45	N + A	0.05 + 0.50	80
	O	0.012	-5
	O + A	0.012 + 0.50	-11
50	O	0.025	-8

TABLE III (Continued)

Treatment	Rate (kg/ha)	% Growth Reduction
O + A	0.025 + 0.50	0
P	0.012	14
P + A	0.012 + 0.50	6
P	0.025	29
P + A	0.025 + 0.50	3
Q	0.012	0
Q + A	0.012 + 0.50	4
Q	0.025	15
Q + A	0.025 + 0.50	7

EXAMPLE 21**Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid as a safener for oat injury from postemergence applications of herbicides**

Oat plants (Porter) approximately 4 to 5 inches tall are sprayed with a formulation of the appropriate herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diammonium salt of 4carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are diluted with water to provide the equivalent of 0.012 kg/ha to 0.50 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 2 to 4 weeks after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table IV wherein

A is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 C is 1-[(o-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-S-triazin-2-yl)urea;
 D is 1-[(o-acetylphenyl)sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea;
 F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
 G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid;
 H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
 I is 3-{p-[3,5-dichloro-2-pyridyl]oxy}phenoxy]-2-hydroxybutyronitrile ethyl carbonate;
 J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate;
 O is 1-[(o-acetylphenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea;
 P is 1-[(o-(cyclopropylcarbonyl)phenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea; and
 Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

TABLE IV

5	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
	C	0.05	22
10	C + A	0.05 + 0.50	12
	C	0.10	34
	C + A	0.10 + 0.50	24
	D	0.025	63
15	D + A	0.025 + 0.50	58
	D	0.05	59
	D + A	0.05 + 0.50	65
	F	0.012	13
20	F + A	0.012 + 0.50	-2
	F	0.025	49
	F + A	0.025 + 0.50	24
25	G	0.012	70
	G + A	0.012 + 0.50	57
	G	0.025	68
30	G + A	0.025 + 0.50	69
	H	0.012	61
	H + A	0.012 + 0.50	41
	H	0.025	67
35	H + A	0.025 + 0.50	69
	I	0.25	3
	I + A	0.25 + 0.50	-2
40	I	0.50	20
	I + A	0.50 + 0.50	3
	J	0.012	51
45	J + A	0.012 + 0.50	47
	J	0.025	54
	J + A	0.025 + 0.50	57
50	O	0.25	37

TABLE IV (Continued)

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<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>% Growth Reduction</u>
O + A	0.25 + 0.50	8
O	0.50	47
O + A	0.50 + 0.50	32
P	0.012	13
P + A	0.012 + 0.50	6
P	0.025	20
P + A	0.025 + 0.50	11
Q	0.025	30
Q + A	0.025 + 0.50	28
Q	0.05	61
Q + A	0.05 + 0.50	40

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EXAMPLE 22**Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid as a safener for spring wheat injury from postemergence applications of herbicides**

Spring wheat plants (Apollo) approximately 4 to 5 inches tall are sprayed with a formulation of the appropriate herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are diluted with water to provide the equivalent of 0.012 kg/ha to 0.50 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 2-4 weeks after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table V wherein

- A is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
- B is methyl o-{3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido}sulfonyl}benzoate;
- C is 1-[(o-chlorophenyl)sulfonyl]-3-(4-methoxy-S-methyl-S-triazin-2-yl)urea;
- D is 1-[(o-acetylphenyl)sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea;
- E is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid;
- F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
- G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid;
- H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
- J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate;
- M is ethyl 2-{p-[(6-chloro-2-benzoxazolyl)oxy]phenoxy}propionate; and
- Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

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TABLE V

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	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
	B	0.075	66
10	B + A	0.075 + 0.50	64
	B	0.10	67
	B + A	0.10 + 0.50	62
	C	0.05	26
15	C + A	0.05 + 0.50	20
	C	0.10	25
	C + A	0.10 + 0.50	25
20	D	0.025	63
	D + A	0.025 + 0.50	56
	D	0.05	60
	D + A	0.05 + 0.50	60
25	E	0.05	21
	E + A	0.05 + 0.50	9
	E	0.10	53
30	E + A	0.10 + 0.50	58
	F	0.025	4
	F + A	0.025 + 0.50	-3
35	F	0.05	2
	F + A	0.05 + 0.50	6
	G	0.012	21
	G + A	0.012 + 0.50	19
40	G	0.025	31
	G + A	0.025 + 0.50	22
	H	0.012	27
45	H + A	0.012 + 0.50	16
	H	0.025	54
	H + A	0.025 + 0.50	50

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TABLE V (Continued)

5	Treatment	Rate (kg/ha)	Growth Reduction
	J	0.012	40
10	J + A	0.012 + 0.50	18
	J	0.025	49
	J + A	0.025 + 0.50	47
	M	0.025	6
15	M + A	0.025 + 0.50	1
	M	0.05	13
	M + A	0.05 + 0.50	10
	Q	0.025	15
20	Q + A	0.025 + 0.50	6
	Q	0.05	30
	Q + A	0.05 + 0.50	15
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EXAMPLE 23**30 Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid as a safener for rice injury from postemergence applications of herbicides**

Rice plants (Tebonnet) approximately 4 to 5 inches tall are sprayed with a formulation of the appropriate herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are diluted with water to provide the equivalent of 0.0015 kg/ha to 0.250 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylarylpolyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 2 to 4 weeks after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table VI wherein

- 45 A is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 B is methyl o-[{3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido}sulfonyl]benzoate;
 C is 1-[o-chlorophenyl]sulfonyl]-3-(4-methoxy-6-methyl-S-triazin-2-yl)urea;
 D is 1-[o-acetylphenyl]sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea;
 F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
 50 G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid;
 H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
 J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate;
 K is 3-(5-tert-butyl-3-isoxazolyl)-4-hydroxy-1-methyl-2-imidazolidinone;
 L is 2-(O-ethyloxime) of 2-butyryl-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one;
 55 M is ethyl 2-{p-[(6-chloro-2-benzoxazolyl)oxy]phenoxy}propionate;
 N is ethyl o-{{[4-chloro-6-methoxy-2-pyrimidinyl]-carbamoyl}sulfamoyl}benzoate;
 P is 1-{o-(cyclopropylcarbonyl)phenyl}sulfamoyl}-3-(4,6-dimethoxy-2-pyrimidinyl)urea; and
 Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

TABLE VI

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	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>\$ Growth Reduction</u>
	B	0.0015	33
10	B + A	0.0015 + 0.50	35
	B	0.003	65
	B + A	0.003 + 0.50	42
	C	0.0015	45
15	C + A	0.0015 + 0.50	35
	C	0.003	42
	C + A	0.003 + 0.50	56
20	D	0.05	40
	D + A	0.05 + 0.50	35
	D	0.10	49
	D + A	0.10 + 0.50	40
25	F	0.003	-3
	F + A	0.003 + 0.50	-6
	F	0.006	5
30	F + A	0.006 + 0.50	-3
	G	0.012	26
	G + A	0.012 + 0.50	12
35	G	0.025	32
	G + A	0.025 + 0.50	60
	H	0.012	47
40	H + A	0.012 + 0.50	43
	H	0.025	57
	H + A	0.025 + 0.50	61
	J	0.012	24
45	J + A	0.012 + 0.50	22
	J	0.025	45
	J + A	0.025 + 0.50	39
50	K	0.05	50

TABLE VI (Continued)

5	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
	K + A	0.05 + 0.50	47
10	K	0.10	49
	K + A	0.10 + 0.50	51
	L	0.025	12
15	L + A	0.025 + 0.50	3
	L	0.05	41
	L + A	0.05 + 0.50	16
	M	0.006	19
20	M + A	0.006 + 0.50	10
	M	0.012	22
	M + A	0.012 + 0.50	22
25	N	0.025	66
	N + A	0.025 + 0.50	66
	N	0.05	63
	N + A	0.05 + 0.50	59
30	P	0.012	20
	P + A	0.012 + 0.50	1
	P	0.025	7
35	P + A	0.025 + 0.50	2
	Q	0.012	6
	Q + A	0.012 + 0.50	15
40	Q	0.025	36
	Q + A	0.025 + 0.50	31

45 **EXAMPLE 24****Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid as a safener for durum (spring) wheat injury from postemergence applications of herbicides**

- 50 Durum (spring) wheat plants (Wakooma) approximately 4 to 5 inches tall are sprayed with a formulation of the appropriate herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are diluted with water to provide the equivalent of 0.003 kg/ha to 0.50 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time.
- 55 The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 2 to 4 weeks after treatment, the tests are terminated and each pot is

examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table VII wherein

- A is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
5 B is methyl o-{[3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido}sulfonyl}benzoate;
C is 1-[(o-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-S-triazin-2-yl)urea;
D is 1-[(o-acetylphenyl)sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea;
F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid;
10 H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate;
K is 3-(5-tert-butyl-3-isoxazolyl)-4-hydroxy-1-methyl-2-imidazolidinone;
L is 2-(O-ethyloxime) of 2-butyryl-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one;
M is ethyl 2-{p-[(6-chloro-2-benzoxazolyl)oxy]phenoxy}propionate;
15 N is ethyl o-{{(4-chloro-6-methoxy-2-pyrimidinyl)-carbamoyl}sulfamoyl}benzoate;
O is 1-[(o-acetylphenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea; and
Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

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TABLE VII

<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
B	0.075	65
B + A	0.075 + 0.50	66
B	0.10	67
B + A	0.10 + 0.50	64
C	0.05	46
C + A	0.05 + 0.50	46
C	0.10	63
C + A	0.10 + 0.50	60
D	0.025	57
D + A	0.025 + 0.50	53
D	0.05	57
D + A	0.05 + 0.50	54
F	0.003	10
F + A	0.003 + 0.50	2
F	0.006	8
F + A	0.006 + 0.50	9
G	0.012	39
G + A	0.012 + 0.50	53
G	0.025	52
G + A	0.025 + 0.50	50
H	0.012	50
H + A	0.012 + 0.50	34
H	0.025	63
H + A	0.025 + 0.50	60
J	0.012	50
J + A	0.012 + 0.50	17
J	0.025	62
J + A	0.025 + 0.50	45
K	0.05	10

TABLE VII (Continued)

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	Treatment	Rate (kg/ha)	Growth Reduction
	K + A	0.05 + 0.50	5
10	K	0.10	28
	K + A	0.10 + 0.50	15
	L	0.10	17
15	L + A	0.10 + 0.50	19
	L	0.25	52
	L + A	0.25 + 0.50	54
	M	0.025	54
20	M + A	0.025 + 0.50	43
	M	0.05	56
	M + A	0.05 + 0.50	61
25	N	0.025	68
	N + A	0.025 + 0.50	67
	N	0.05	68
	N + A	0.05 + 0.50	71
30	O	0.25	27
	O + A	0.25 + 0.50	25
	O	0.50	42
35	O + A	0.50 + 0.50	33
	Q	0.025	35
	Q + A	0.025 + 0.50	43
40	Q	0.05	66
	Q + A	0.05 + 0.50	51

45 **EXAMPLE 25****Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-aceticacid as a safener for winter barley injury from postemergence applications of herbicides**

- 50 Winter barley plants (Marinka) approximately 4 to 5 inches tall are sprayed with a formulation of the appropriate herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are diluted with water to provide the equivalent of 0.012 kg/ha to 0.50 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time.
- 55 The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 2 to 4 weeks after treatment, the tests are terminated and each pot is

examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table VIII wherein

- 5 A is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
- C is 1-[(o-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-S-triazin-2-yl)urea;
- D is 1-[(o-acetylphenyl)sulfamoyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea;
- E is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid;
- F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
- H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
- 10 I is 3-{p-[(3,5-dichloro-2-pyridyl)oxy]phenoxy}-2-hydroxybutyronitrile ethyl carbonate;
- J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate;
- K is 3-(5-tert-butyl-3-isoxazolyl)-4-hydroxy-1-methyl-2-imidazolidinone;
- L is 2-(O-ethyloxime) of 2-butyryl-5-[2-(ethylthio)-propyl]-3-hydroxy-2-cyclohexen-1-one;
- O is 1-[(o-acetylphenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea;
- 15 P is 1-{[o-(cyclopropylcarbonyl)phenyl]sulfamoyl}-3-(4,6-dimethoxy-2-pyrimidinyl)urea; and
- Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

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TABLE VIII

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<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
C	0.05	4
C + A	0.05 + 0.50	13
C	0.10	34
C + A	0.10 + 0.50	16
D	0.025	60
D + A	0.025 + 0.50	54
D	0.05	61
D + A	0.05 + 0.50	61
E	0.05	61
E + A	0.05 + 0.50	56
E	0.075	61
E + A	0.075 + 0.50	61
F	0.05	37
F + A	0.05 + 0.50	20
F	0.10	53
F + A	0.10 + 0.50	56
H	0.012	40
H + A	0.012 + 0.50	31
H	0.025	60
H + A	0.025 + 0.50	55
I	0.25	5
I + A	0.25 + 0.50	-10
I	0.50	-7
I + A	0.50 + 0.50	-11
J	0.012	56
J + A	0.012 + 0.50	28
J	0.025	58
J + A	0.025 + 0.50	59
K	0.05	5

TABLE VIII (Continued)

	Treatment	Rate (kg/ha)	% Growth Reduction
5	K + A	0.05 + 0.50	0
	K	0.10	18
10	K + A	0.10 + 0.50	22
	L	0.10	12
	L + A	0.10 + 0.50	16
15	L	0.25	36
	L + A	0.25 + 0.50	31
	O	0.25	27
20	O + A	0.25 + 0.50	25
	O	0.50	42
	O + A	0.50 + 0.50	33
	P	0.012	13
25	P + A	0.012 + 0.50	9
	P	0.025	14
	P + A	0.025 + 0.50	9
30	Q	0.025	21
	Q + A	0.025 + 0.50	9
	Q	0.05	33
35	Q + A	0.05 + 0.50	28

EXAMPLE 26**40 Evaluation of the diammonium salt of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid as a safener for cotton Injury from postemergence applications of herbicides**

Cotton plants (825) at the cotyledon stage are sprayed with a formulation of the appropriate herbicide, or a formulation of the appropriate herbicide mixed with a formulation of the diammonium salt of 4-carboxy-45 3,4-dihydro-2H-1-benzopyran-4-acetic acid. The herbicide and safener are diluted with water to provide the equivalent of 0.0015 kg/ha to 0.10 kg/ha of herbicide and 0.50 kg/ha of safener to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on 50 greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 2 to 4 weeks after treatment, the tests are terminated and the foliage is clipped and dried. The dry clipping weight results are averaged and expressed as a percent growth reduction compared to an untreated check, using the following formula:

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$$\text{% Growth Reduction} = 100 - \left[\frac{\text{Dry Weight of Treated Plants}}{\text{Dry Weight of Untreated Plants}} \times 100 \right]$$

The results are summarized in Table IX wherein

- A is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 B is methyl o-{{3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido}sulfonyl}benzoate;
 C is 1-[(o-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-S-triazin-2-yl)urea;
 5 E is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid;
 F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
 H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
 J is methyl (RS)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate; and
 Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

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TABLE IX

	Treatment	Rate (kg/ha)	% Growth Reduction
15	B	0.0015	23
	B + A	0.0015 + 0.50	4
	B	0.003	4
	B + A	0.003 + 0.50	25
20	C	0.0015	93
	C + A	0.0015 + 0.50	77
	C	0.003	92
	C + A	0.003 + 0.50	89
	E	0.05	58
25	E + A	0.05 + 0.50	51
	E	0.075	57
	E + A	0.075 + 0.50	55
	F	0.05	76
30	F + A	0.05 + 0.50	56
	F	0.10	72
	F + A	0.10 + 0.50	82
	H	0.012	60
	H + A	0.012 + 0.50	18
35	H	0.025	73
	H + A	0.025 + 0.50	51
	J	0.012	23
	J + A	0.012 + 0.50	6
	J	0.025	9
40	J + A	0.025 + 0.50	3
	Q	0.012	60
	Q + A	0.012 + 0.50	61
	Q	0.025	78
	Q + A	0.025 + 0.50	76

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EXAMPLE 27Evaluation of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to corn caused by postemergence applications of herbicides

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Corn seeds (Pioneer 3475) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid by first making a stock solution of 100 mg of the safener in 2.5 mL of an acetone:dimethylformamide (5:1) mixture. Aliquots of the stock solution ranging from 62.5 μ L to 1.0 mL are made up to 1 mL with an acetone:dimethylformamide (10:1) mixture, added to 10 g of corn seed and shaken thoroughly to provide seed treatment rates equivalent to 0.25 to 4.0 mg of safener per gram of seed. Seeds are dried, planted in soil, placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. At the 2 to 3 leaf stage, the corn plants are sprayed with a herbicide solution. The herbicide spray solution is diluted with water to provide the equivalent of 0.006 to 0.05 kg/ha of herbicide to the

foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered after 48 hours and cared for in accordance with conventional greenhouse procedures. After 14 days, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table X wherein,

- A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 10 F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
 E is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid; and
 H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

TABLE X

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	Treatment	Rate		% Growth Reduction
		(kg/ha)	(mg/g of seed)	
20	F	0.05		60
	F + A	0.05	0.25	52
	F + A	0.05	0.50	52
	F + A	0.05	1.0	40
	F + A	0.05	2.0	35
	F + A	0.05	4.0	29
25	E	0.025		35
	E + A	0.025	0.25	10
	E + A	0.025	0.50	31
	E + A	0.025	1.0	20
	E + A	0.025	2.0	11
	E + A	0.025	4.0	-5
30	E	0.05		64
	E + A	0.05	0.25	48
	E + A	0.05	0.50	57
	E + A	0.05	1.0	65
	E + A	0.05	2.0	46
	E + A	0.05	4.0	11
35	H	0.006		12
	H + A	0.006	0.25	6
	H + A	0.006	0.50	3
	H + A	0.006	1.0	2
	H + A	0.006	2.0	-6
	H + A	0.006	4.0	-13
40	H	0.012		42
	H + A	0.012	0.25	57
	H + A	0.012	0.50	60
	H + A	0.012	1.0	47
	H + A	0.012	2.0	42
	H + A	0.012	4.0	23
45	H + A	0.012		

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EXAMPLE 28**Evaluation of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to barley caused by postemergence applications of herbicides**

Barley seeds (Volga) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid by first making a stock solution of 100 mg of the safener in 2.5 mL of an acetone:dimethylformamide (5:1)

mixture. Aliquots of the stock solution ranging from 62.5 μ L to 1.0 mL are made up to 1 mL with an acetone:dimethylformamide (10:1) mixture, added to 10 g of barley seed and shaken thoroughly to provide seed treatment rates equivalent to 0.25 to 4.0 mg of safener per gram of seed. Seeds are dried, planted in soil, placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. At the 1 to 2 leaf stage, the barley plants are sprayed with a herbicide solution. The herbicide spray solution is diluted with water to provide the equivalent of 0.006 to 0.1 kg/ha of herbicide to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered after 48 hours and cared for in accordance with conventional greenhouse procedures. After 14 days, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an, untreated check, as described in example 18.

The results are summarized in Table XI wherein

- A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
H is isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate; and
M is ethyl 2-{p-[(6-chloro-2-benzoxazolyl)oxy]phenoxy}propionate.

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TABLE XI

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	<u>Treatment</u>	<u>Rate</u>		<u>% Growth Reduction</u>
		<u>(kg/ha)</u>	<u>(mg/g of seed)</u>	
	H	0.006		31
10	H + A	0.006	0.25	28
	H + A	0.006	0.50	16
	H + A	0.006	1.0	21
15	H + A	0.006	2.0	22
	H + A	0.006	4.0	22
	H	0.012		65
20	H + A	0.012	0.25	68
	H + A	0.012	0.50	64
	H + A	0.012	1.0	67
25	H + A	0.012	2.0	64
	H + A	0.012	4.0	69
	H	0.025		66
	H + A	0.025	0.25	66
30	H + A	0.025	0.50	65
	H + A	0.025	1.0	63
	H + A	0.025	2.0	66
35	H + A	0.025	4.0	67
	M	0.025		-1
	M + A	0.025	0.25	-5
40	M + A	0.025	0.50	-4
	M + A	0.025	1.0	-6
	M + A	0.025	2.0	-4
	M	0.050		8
45	M + A	0.050	0.25	1
	M + A	0.050	0.50	3
	M + A	0.050	1.0	3
50	M + A	0.050	2.0	3

TABLE XI (Continued)

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	Treatment	Rate		% Growth Reduction
		(kg/ha)	(mg/g of seed)	
10	M	0.10		20
10	M + A	0.10	0.25	8
	M + A	0.10	0.50	11
	M + A	0.10	1.0	11
15	M + A	0.10	2.0	2

EXAMPLE 29

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Evaluation of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to sorghum caused by postemergence application of 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid

25 Sorghum seeds (NC 271) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid by first making a stock solution of 100 mg of the safener in 2.5 mL of acetone:dimethylformamide (5:1) mixture. Aliquots of the stock solution ranging from 62.5 μ L to 1.0 mL are made up to 1 mL with an acetone:dimethylformamide (10:1) mixture, added to 10 g of sorghum seed and shaken thoroughly to provide seed treatment rates equivalent to 0.25 to 4.0 mg of safener per gram of seed. Seeds are dried, planted in soil, placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. At the 2 to 3 leaf stage, the sorghum plants are sprayed with a 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid formulation. The 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid spray formulation is diluted with water to provide the equivalent of 0.01 to 0.025 kg/ha of 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid spray formulation contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered after 48 hours and cared for in accordance with conventional greenhouse procedures.

30 After 14 days, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

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The results are summarized in Table XII wherein

A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid; and

45 G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid.

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TABLE XII

	Treatment	Rate		% Growth Reduction
		(kg/ha)	(mg/g of seed)	
5	G	0.01		17
	G + A	0.01	0.25	15
	G + A	0.01	0.50	7
	G + A	0.01	1.0	-2
	G + A	0.01	2.0	-1
	G + A	0.01	4.0	-14
	G	0.025		30
	G + A	0.025	0.25	41
	G + A	0.025	0.50	38
	G + A	0.025	1.0	45
10	G + A	0.025	2.0	16
	G + A	0.025	4.0	15
15	G	0.025		30
	G + A	0.025	0.25	41
	G + A	0.025	0.50	38
	G + A	0.025	1.0	45
	G + A	0.025	2.0	16
	G + A	0.025	4.0	15
	G	0.025		30
	G + A	0.025	0.25	41
	G + A	0.025	0.50	38
	G + A	0.025	1.0	45

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EXAMPLE 30Evaluation of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to oats caused by postemergence application of methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate

Tame oat seeds (Porter) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid by first making a stock solution of 100 mg of the safener in 2.5 mL of an acetone:dimethylformamide (5:1) mixture. Aliquots of the stock solution ranging from 62.5 µL to 1.0 mL are made up to 1 mL with an acetone:dimethylformamide (10:1) mixture, added to 10 g of oat seed and shaken thoroughly to provide seed treatment rates equivalent to 0.25 to 4.0 mg of safener per gram of seed. Seeds are dried, planted in soil, placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. At the 2 leaf stage, the oat plants are sprayed with a methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate solution. The methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate spray solution is diluted with water to provide the equivalent of 0.025 to 0.05 kg/ha of methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylarylpolyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered after 48 hours and cared for in accordance with conventional greenhouse procedures. After 14 days, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table XIII wherein

A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid; and
Q is methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate.

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TABLE XIII

Treatment	Rate		% Growth Reduction
	(kg/ha)	(mg/g of seed)	
Q	0.025		41
Q + A	0.025	0.25	28
Q + A	0.025	0.50	17
Q + A	0.025	1.0	31
Q + A	0.025	2.0	30
Q + A	0.025	4.0	28
Q	0.05		50
Q + A	0.05	0.25	46
Q + A	0.05	0.50	43
Q + A	0.05	1.0	45
Q + A	0.05	2.0	44
Q + A	0.05	4.0	53

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EXAMPLE 31**Evaluation of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to rice caused by postemergence application of 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid**

Rice seeds (Tebonnet) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid by first making a stock solution of 100 mg of the safener in 2.5 mL of an acetone:dimethylformamide (5:1) mixture. Aliquots of the stock solution ranging from 62.5 μ L to 1.0 mL are made up to 1 mL with an acetone:dimethylformamide (10:1) mixture, added to 10 g of rice seed and shaken thoroughly to provide seed treatment rates equivalent to 0.25 to 4.0 mg of safener per gram of seed. Seeds are dried, planted in soil, placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. At the 1 to 2 leaf stage, the rice plants are sprayed with a 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid formulation. The 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid spray formulation is diluted with water to provide the equivalent of 0.01 to 0.025 kg/ha of 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid spray formulation contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered after 48 hours and cared for in accordance with conventional greenhouse procedures. After 14 days, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in Example 18.

The results are summarized in Table XIV wherein

A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid; and
 G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid.

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TABLE XIV

	Treatment	Rate		% Growth Reduction
		(kg/ha)	(mg/g of seed)	
5	G	0.01		24
10	G + A	0.01	0.25	4
15	G + A	0.01	0.50	-5
20	G + A	0.01	1.0	-3
25	G + A	0.01	2.0	-9
30	G + A	0.01	4.0	-6
35	G	0.025		49
40	G + A	0.025	0.25	59
45	G + A	0.025	0.50	40
50	G + A	0.025	1.0	49
55	G + A	0.025	2.0	41
60	G + A	0.025	4.0	37

EXAMPLE 32**Evaluation of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to corn caused by preemergence applications of herbicides**

Corn seeds (Pioneer 3475) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid by first making a stock solution of 100 mg of the safener in 2.5 mL of an acetone:dimethylformamide (5:1) mixture. Aliquots of the stock solution ranging from 62.5 μ L to 1.0 mL are made up to 1 mL with an acetone:dimethylformamide (10:1) mixture, added to 10 g of corn seed and shaken thoroughly to provide seed treatment rates equivalent to 0.25 to 4.0 mg of safener per gram of seed. Seeds are dried and planted in soil. The soil surface is moistened and sprayed preemergence with a herbicide solution. The herbicide spray solution is diluted with water to provide the equivalent of 0.032 to 4.0 kg/ha of herbicide to the soil surface when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures.

Twenty-one days after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table XV wherein

A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;

F is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;

45 G is 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolnecarboxylic acid; and

R is 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide; and

S is N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine.

TABLE XV

Treatment	(kg/ha)	Rate (mg/g of seed)	% Growth Reduction
F	0.1		79
F + A	0.1	0.25	53
F + A	0.1	0.50	62
F + A	0.1	1.0	55
F + A	0.1	2.0	50
F + A	0.1	4.0	39
G	0.032		74
G + A	0.032	0.25	71
G + A	0.032	0.50	82
G + A	0.032	1.0	71
G + A	0.032	2.0	67
G + A	0.032	4.0	38
R	2.0		38
R + A	2.0	0.25	25
R + A	2.0	0.50	2
R + A	2.0	1.0	-1
R + A	2.0	2.0	-8
R + A	2.0	4.0	-4
R	4.0		53
R + A	4.0	0.25	35
R + A	4.0	0.50	23
R + A	4.0	1.0	16
R + A	4.0	2.0	8
R + A	4.0	4.0	12
S	2.5		20
S + A	2.5	0.25	18
S + A	2.5	0.50	3
S + A	2.5	1.0	7
S + A	2.5	2.0	15

EXAMPLE 33**Evaluation of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to oats caused by preemergence applications of herbicides**

Tame oat seeds (Porter) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid by first making a stock solution of 100 mg of the safener in 2.5 mL of an acetone:dimethylformamide (5:1) mixture. Aliquots of the stock solution ranging from 25.0 μ L to 0.5 mL are made up to 1 mL with an acetone:dimethylformamide (10:1) mixture, added to 10 g of seed and shaken thoroughly to provide seed treatment rates equivalent to 0.10 to 2.0 mg of safener per gram of seed. Seeds are dried and planted in soil. The soil surface is moistened and sprayed preemergence with a herbicide solution. The herbicide spray solution is diluted with water to provide the equivalent of 0.50 to 2.0 kg/ha of herbicide to the soil surface when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures.

Twenty-one days after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table XVI wherein
A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
R is 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide; and
T is ethyl dipropylthiocarbamate.

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TABLE XVI

Treatment	Rate		% Growth Reduction
	(kg/ha)	(mg/g of seed)	
R	1.0		34
R + A	1.0	0.10	40
R + A	1.0	0.25	40
R + A	1.0	0.50	40
R + A	1.0	1.00	38
R + A	1.0	2.00	26
R	2.0		69
R + A	2.0	0.10	57
R + A	2.0	0.25	44
R + A	2.0	0.50	54
R + A	2.0	1.00	50
R + A	2.0	2.00	42
T	0.5		18
T + A	0.5	0.10	20
T + A	0.5	0.25	8
T + A	0.5	0.50	15
T + A	0.5	1.00	10
T + A	0.5	2.00	-7
T	1.0		61
T + A	1.0	0.10	74
T + A	1.0	0.50	67
T + A	1.0	1.00	55
T + A	1.0	2.00	49

EXAMPLE 34

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Evaluation of 4-Carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to wheat caused by preemergence application of 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide

Wheat seeds (Wakooma) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid by first making a stock solution of 100 mg of the safener in 2.5 mL of an acetone:dimethylformamide (5:1) mixture. Aliquots of the stock solution ranging from 25.0 μ L to 0.5 mL are made up to 1 mL with an acetone:dimethylformamide (10:1) mixture, added to 10 g of wheat seed and shaken thoroughly to provide seed treatment rates equivalent to 0.10 to 2.0 mg of safener per gram of seed. Seeds are dried and planted in soil. The soil surface is moistened and sprayed preemergence with a 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide solution. The 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide spray solution is diluted with water to provide the equivalent of 0.30 to 0.60 kg/ha of 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide to the soil surface when applied through a spray nozzle operating at 40 psi for a predetermined time. The 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide

spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures.

- 5 Twenty-one days after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table XVII wherein

- A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid; and
10 R is 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide.

TABLE XVII

	Treatment	Rate		% Growth Reduction
		(kg/ha)	(mg/g of seed)	
15	R	0.30		64
	R + A	0.30	0.10	70
	R + A	0.30	0.25	58
	R + A	0.30	0.50	62
	R + A	0.30	1.00	55
	R + A	0.30	2.00	38
	R	0.60		75
	R + A	0.60	0.10	88
	R + A	0.60	0.25	77
	R + A	0.60	0.50	80
20	R + A	0.60	1.00	76
	R + A	0.60	2.00	63
25	R	0.60		75
	R + A	0.60	0.10	88
	R + A	0.60	0.25	77
	R + A	0.60	0.50	80
	R + A	0.60	1.00	76
	R + A	0.60	2.00	63
	R	0.60		75
	R + A	0.60	0.10	88
	R + A	0.60	0.25	77
	R + A	0.60	0.50	80
30	R + A	0.60	1.00	76
	R + A	0.60	2.00	63

EXAMPLE 35

- 35 **Evaluation of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for injury to corn caused by pre-plant incorporation of herbicides**

Three inch square pots are filled with 150 mL of Sassafras soil containing 17% sand and sprayed with a herbicide solution. The herbicide spray solution is diluted with water to provide the equivalent of 1.0 to 4.0 kg/ha of herbicide to the soil surface when applied through a spray nozzle operating at 40 psi for a predetermined time. After the soil is sprayed, it is poured into a plastic basin and mixed. The pots are refilled with 100 mL of the treated soil. Corn seeds (Pioneer 3475) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid according to the procedure described in example 27, planted in the treated soil and covered with the remaining 50 mL of treated soil. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures.

40 Twenty-one days after planting, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table XVIII wherein

- 45 A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
50 R is 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide; and
S is N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine.

TABLE XVIII

	Treatment	Rate		% Growth Reduction
		(kg/ha)	(mg/g of seed)	
5	R	2.0		21
	R + A	2.0	0.10	13
	R + A	2.0	0.25	-5
	R + A	2.0	0.50	0
	R + A	2.0	1.00	2
	R + A	2.0	2.00	16
	R	4.0		38
	R + A	4.0	0.10	14
	R + A	4.0	0.25	17
	R + A	4.0	0.50	10
10	R + A	4.0	1.00	6
	R + A	4.0	2.00	3
	S	1.0		18
	S + A	1.0	0.10	-10
	S + A	1.0	0.25	-17
	S + A	1.0	0.50	-10
	S + A	1.0	1.0	-11
	S + A	1.0	2.0	-6
	S	2.0		26
	S + A	2.0	0.10	23
15	S + A	2.0	0.25	2
	S + A	2.0	0.50	6
	S + A	2.0	1.0	6
	S + A	2.0	2.0	8
	R	4.0		38
	R + A	4.0	0.10	14
	R + A	4.0	0.25	17
	R + A	4.0	0.50	10
	R + A	4.0	1.00	6
	R + A	4.0	2.00	3
20	S	1.0		18
	S + A	1.0	0.10	-10
	S + A	1.0	0.25	-17
	S + A	1.0	0.50	-10
	S + A	1.0	1.0	-11
	S + A	1.0	2.0	-6
	S	2.0		26
	S + A	2.0	0.10	23
	S + A	2.0	0.25	2
	S + A	2.0	0.50	6
25	S + A	2.0	1.0	6
	S + A	2.0	2.0	8
	R	4.0		38
	R + A	4.0	0.10	14
	R + A	4.0	0.25	17
	R + A	4.0	0.50	10
	R + A	4.0	1.00	6
	R + A	4.0	2.00	3
	S	1.0		18
	S + A	1.0	0.10	-10
30	S + A	1.0	0.25	-17
	S + A	1.0	0.50	-10
	S + A	1.0	1.0	-11
	S + A	1.0	2.0	-6
	S	2.0		26
	S + A	2.0	0.10	23
	S + A	2.0	0.25	2
	S + A	2.0	0.50	6
	S + A	2.0	1.0	6
	S + A	2.0	2.0	8

EXAMPLE 36**35 Evaluation of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for Injury to barley caused by pre-plant incorporation of herbicides**

Three inch square pots are filled with 150 mL of Sassafras soil containing 17% sand and sprayed with a herbicide solution. The herbicide spray solution is diluted with water to provide the equivalent of 0.50 to 4.0 kg/ha of herbicide to the soil surface when applied through a spray nozzle operating at 40 psi for a predetermined time. After the soil is sprayed, it is poured into a plastic basin and mixed. The pots are refilled with 100 mL of the treated soil. Barley seeds (Volga) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid according to the procedure described in example 28, planted in the treated soil and covered with the remaining 50 mL of treated soil. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures.

Twenty-one days after planting, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table XIX wherein

- 50 A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 R is 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide; and
 T is ethyl dipropylthiocarbamate.

TABLE XIX

Treatment	(kg/ha)	Rate (mg/g of seed)	% Growth Reduction
R	2.0		54
R + A	2.0	0.10	61
R + A	2.0	0.25	74
R + A	2.0	0.50	56
R + A	2.0	1.00	49
R + A	2.0	2.00	47
R	4.0		72
R + A	4.0	0.10	81
R + A	4.0	0.25	71
R + A	4.0	0.50	71
R + A	4.0	1.00	65
R + A	4.0	2.00	63
T	0.5		50
T + A	0.5	0.10	27
T + A	0.5	0.25	42
T + A	0.5	0.50	16
T + A	0.5	1.00	20
T + A	0.5	2.00	31
T	1.0		86
T + A	1.0	0.10	96
T + A	1.0	0.25	38
T + A	1.0	0.50	37
T + A	1.0	1.00	47
T + A	1.0	2.00	31

EXAMPLE 37

**Evaluation of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid applied as a seed treatment for
Injury to oats caused by pre-plant incorporation of herbicides**

Three inch square pots are filled with 150 mL of Sassafras soil containing 17% sand and sprayed with a herbicide solution. The herbicide spray solution is diluted with water to provide the equivalent of 0.125 to 3.0 kg/ha of herbicide to the soil surface when applied through a spray nozzle operating at 40 psi for a predetermined time. After the soil is sprayed, it is poured into a plastic basin and mixed. The pots are refilled with 100 mL of the treated soil. Oat seeds (Porter) are treated with the safener 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid according to the procedure described in example 32, planted in the treated soil and covered with the remaining 50 mL of treated soil. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures.

Twenty-one days after planting, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

- The results are summarized in Table XX wherein
- A is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - R is 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide; and
 - T is ethyl dipropylthiocarbamate.

TABLE XX

	Treatment	Rate		% Growth Reduction
		(kg/ha)	(mg/g of seed)	
5	R	1.5		70
	R + A	1.5	0.10	73
	R + A	1.5	0.25	51
	R + A	1.5	0.50	46
	R + A	1.5	1.00	58
	R + A	1.5	2.00	36
	R	3.0		86
	R + A	3.0	0.10	86
	R + A	3.0	0.25	84
	R + A	3.0	0.50	80
10	R + A	3.0	1.00	76
	R + A	3.0	2.00	72
	T	0.125		45
	T + A	0.125	0.10	27
	T + A	0.125	0.25	28
	T + A	0.125	0.50	32
	T + A	0.125	1.00	32
	T + A	0.125	2.00	20
	T	0.25		88
	T + A	0.25	0.10	80
15	T + A	0.25	0.25	71
	T + A	0.25	0.50	87
	T + A	0.25	1.00	87
	T + A	0.25	2.00	76
	T	0.25		88
	T + A	0.25	0.10	80
	T + A	0.25	0.25	71
	T + A	0.25	0.50	87
	T + A	0.25	1.00	87
	T + A	0.25	2.00	76
20	T	0.25		88
	T + A	0.25	0.10	80
	T + A	0.25	0.25	71
	T + A	0.25	0.50	87
	T + A	0.25	1.00	87
	T	0.25		88
	T + A	0.25	0.10	80
	T + A	0.25	0.25	71
	T + A	0.25	0.50	87
	T + A	0.25	1.00	87
25	T	0.25		88
	T + A	0.25	0.10	80
	T + A	0.25	0.25	71
	T + A	0.25	0.50	87
	T + A	0.25	1.00	87
	T	0.25		88
	T + A	0.25	0.10	80
	T + A	0.25	0.25	71
	T + A	0.25	0.50	87
	T + A	0.25	1.00	87
30	T	0.25		88
	T + A	0.25	0.10	80
	T + A	0.25	0.25	71
	T + A	0.25	0.50	87
	T + A	0.25	1.00	87
	T	0.25		88
	T + A	0.25	0.10	80
	T + A	0.25	0.25	71
	T + A	0.25	0.50	87
	T + A	0.25	1.00	87

EXAMPLE 38

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Evaluation of test compounds as safeners for corn injury from postemergence applications of 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid

40 Corn plants (Pioneer 3475) in the third leaf stage are sprayed with a solution of 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid, or a solution of 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid mixed with a solution of a test compound. The 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid and test compound solutions are diluted with water to provide the equivalent of 0.05 kg/ha of 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid and 0.032 to 0.50 kg/ha of test compound to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From 3 to 4 weeks after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

45 The results are summarized in Tables XXI and XXII. The tests reported in Table XXI are terminated 27 days after treatment and the tests reported in Table XXII are terminated 26 days after treatment.

In Tables XXI and XXII

- 50 A is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;
B is the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
C is 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
D is 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzopyran-4-acetate, diethyl ester;

E is 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 F is 4-carboxy-8-chloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 G is 4-carboxy-6,8-dichloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 H is 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-acetic acid;
 5 I is 4-carboxy-3,4-dihydro-2H-1-benzothiopyran-4-acetic acid;
 J is 4-carboxy-6-fluoro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 K is 4-carboxy-6-fluoro-3,4-dihydro-2-methyl-2H-1-benzopyran-4-acetic acid, mixture of dia-
 stereomers;
 L is 6-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 10 M is 7-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 N is 8-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 O is 4-carboxy-6,8-dibromo-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 P is 4-carboxy-6-[(2-chloro- $\alpha,\alpha,\alpha,6$ -tetrafluoro-p-tolyl)oxy]-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 Q is 4-carboxy-3,4-dihydro-6-methoxy-2H-1-benzopyran-4-acetic acid;
 15 R is 4-carboxy-6,8-dimethyl-3,4-dihydro-2H-1-benzopyran-4-acetic acid; and
 S is 2,2',3,3',4',5'-hexahydrospiro[2H-1-benzopyran-4,3'(2'H)-furan]-2',5'-dione.

TABLE XXI

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<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
A	0.05	49
25 B + A	0.032 + 0.05	27
B + A	0.063 + 0.05	22
B + A	0.125 + 0.05	18
30 B + A	0.25 + 0.05	16
B + A	0.50 + 0.05	17
C + A	0.032 + 0.05	26
35 C + A	0.063 + 0.05	19
C + A	0.125 + 0.05	19
C + A	0.25 + 0.05	17
40 C + A	0.50 + 0.05	13
D + A	0.032 + 0.05	19
D + A	0.063 + 0.05	47
45 D + A	0.125 + 0.05	36
D + A	0.25 + 0.05	38
D + A	0.50 + 0.05	36
E + A	0.032 + 0.05	10
50 E + A	0.063 + 0.05	26
E + A	0.125 + 0.05	26
E + A	0.25 + 0.05	13
55 E + A	0.50 + 0.05	8
F + A	0.032 + 0.05	42

TABLE XXI (Continued)

	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>% Growth Reduction</u>
5	F + A	0.063 + 0.05	31
10	F + A	0.125 + 0.05	26
15	F + A	0.25 + 0.05	21
20	F + A	0.50 + 0.05	17
25	G + A	0.032 + 0.05	38
30	G + A	0.063 + 0.05	16
35	G + A	0.125 + 0.05	17
40	G + A	0.25 + 0.05	23
45	G + A	0.50 + 0.05	12
50	H + A	0.032 + 0.05	50
	H + A	0.063 + 0.05	39
	H + A	0.125 + 0.05	37
	H + A	0.25 + 0.05	31
	H + A	0.50 + 0.05	13
	I + A	0.032 + 0.05	56
	I + A	0.063 + 0.05	38
	I + A	0.125 + 0.05	21
	I + A	0.25 + 0.05	9
	I + A	0.50 + 0.05	5
	J + A	0.032 + 0.05	35
	J + A	0.063 + 0.05	13
	J + A	0.125 + 0.05	8
	J + A	0.25 + 0.05	22
	J + A	0.50 + 0.05	11
	K + A	0.032 + 0.05	46
	K + A	0.063 + 0.05	51
	K + A	0.125 + 0.05	46
	K + A	0.25 + 0.05	15
	K + A	0.50 + 0.05	26

TABLE XXII

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<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
A	0.05	33
B + A	0.032 + 0.05	22
B + A	0.063 + 0.05	17
B + A	0.125 + 0.05	23
B + A	0.25 + 0.05	20
B + A	0.50 + 0.05	20
C + A	0.032 + 0.05	19
C + A	0.063 + 0.05	19
C + A	0.125 + 0.05	18
C + A	0.25 + 0.05	12
C + A	0.50 + 0.05	4
L + A	0.032 + 0.05	27
L + A	0.063 + 0.05	29
L + A	0.125 + 0.05	25
L + A	0.25 + 0.05	23
L + A	0.50 + 0.05	18
M + A	0.032 + 0.05	56
M + A	0.063 + 0.05	48
M + A	0.125 + 0.05	26
M + A	0.25 + 0.05	11
M + A	0.50 + 0.05	16
N + A	0.032 + 0.05	46
N + A	0.063 + 0.05	37
N + A	0.125 + 0.05	32
N + A	0.25 + 0.05	21
N + A	0.50 + 0.05	17
O + A	0.032 + 0.05	27
O + A	0.063 + 0.05	25
O + A	0.125 + 0.05	45

TABLE XXII (Continued)

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	<u>Treatment</u>	<u>Rate (kg/ha)</u>	<u>Growth Reduction</u>
	O + A	0.2550 + 0.05	15
	O + A	0.50 + 0.05	14
10	P + A	0.032 + 0.05	39
	P + A	0.063 + 0.05	44
	P + A	0.125 + 0.05	32
15	P + A	0.25 + 0.05	52
	P + A	0.50 + 0.05	41
	Q + A	0.032 + 0.05	39
20	Q + A	0.063 + 0.05	55
	Q + A	0.125 + 0.05	22
	Q + A	0.25 + 0.05	18
	Q + A	0.50 + 0.05	20
25	R + A	0.032 + 0.05	37
	R + A	0.063 + 0.05	49
	R + A	0.125 + 0.05	34
30	R + A	0.25 + 0.05	59
	R + A	0.50 + 0.05	16
	S + A	0.032 + 0.05	47
35	S + A	0.063 + 0.05	18
	S + A	0.125 + 0.05	27
	S + A	0.25 + 0.05	12
40	S + A	0.50 + 0.05	9

EXAMPLE 39

45 Evaluation of 1-carboxy-1,2,3,4-tetrahydro-1-naphthaleneacetic acid as a safener for corn injury from postemergence applications of 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-nicotinic acid

Corn plants (Pioneer 3475) in the third leaf stage are sprayed with a solution of 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid, or a solution of 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid mixed with a solution of 1-carboxy-1,2,3,4-tetrahydro-1-naphthaleneacetic acid. The 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid and 1-carboxy-1,2,3,4-tetrahydro-1-naphthaleneacetic acid solutions are diluted with water to provide the equivalent of 0.05 kg/ha of 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid and 0.032 to 0.50 kg/ha of 1-carboxy-1,2,3,4-tetrahydro-1-naphthaleneacetic acid to the foliage when applied through a spray nozzle operating at 40 psi for a predetermined time. The herbicide spray solution contains 0.25% of the spray adjuvant ORTHO X-77, a non-ionic wetting agent containing alkylaryl polyoxyethylene, glycols, free fatty acids and isopropanol, manufactured by Valent USA Corp. Pots are then placed on greenhouse benches, watered and cared for in

accordance with conventional greenhouse procedures. Thirty days after treatment, the tests are terminated and each pot is examined and rated by measuring the height of the foliage. The test results are averaged and expressed as a percent growth reduction compared to an untreated check, as described in example 18.

The results are summarized in Table XXIII wherein

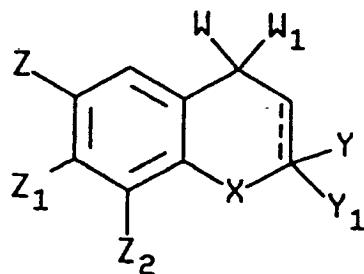
- 5 A is 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid; and
T is 1-carboxy-1,2,3,4-tetrahydro-1-naphthaleneacetic acid.

TABLE XXIII

Treatment	Rate (kg/ha)	% Growth Reduction
A	0.05	37
T + A	0.032 + 0.05	75
T + A	0.063 + 0.05	79
T + A	0.125 + 0.05	73
T + A	0.25 + 0.05	44
T + A	0.50 + 0.05	31

Claims

- 25 1. A method for protecting crops from injury caused by a herbicidally effective amount of a herbicide which is characterized by applying to the crop plant, the seed of the crop, or the soil or water surrounding the crop or crop seed an effective antidotal amount of a safener compound having the structural formula



wherein

- | | | |
|----|---|--|
| 40 | X is
q is
Z, Z_1 and Z_2 are | O, S(O) _q or CH ₂ ;
an integer of 0, 1 or 2;
each independently hydrogen,
halogen, C ₃ -C ₁₀ alkenyl, C ₃ -C ₁₀ alkynyl,
furyl, C ₁ -C ₇ alkoxy, C ₃ -C ₁₀ alkenyloxy,
Z ₃ C(O), Z ₄ S(O) _p , |
| 45 | | C ₁ -C ₁₀ alkyl optionally substituted with one or more halogen atoms,
hydroxy groups, amino groups, thio groups, C ₁ -C ₅ alkylcarbonyl groups or
C ₁ -C ₅ alkoxy groups, or |
| 50 | | phenoxy optionally substituted with one or more halogen atoms or
C ₁ -C ₄ alkyl groups optionally substituted with one or more halogen atoms; |
| 55 | Z ₃ is
Z ₄ is
p is
Y and Y ₁ are
--- | C ₁ -C ₆ alkyl;
C ₁ -C ₆ alkyl;
an integer of 0, 1 or 2;
each independently hydrogen,
C ₁ -C ₆ alkyl, halogen, phenyl, C ₁ -C ₆ alkoxy, amino or C ₁ -C ₆ alkylcarbonyl;
represents a single or double bond with the proviso that when <u>—</u> represents a
double bond then Y ₁ is not present;
W and W ₁ are |
| | | each independently (CRR ₁) _A , and when taken together with the carbon atom |

to which they are attached W and W₁ may form a ring in which WW₁ is represented by the structure:



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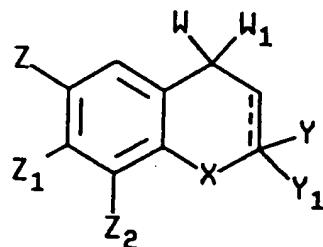
	n is	with the proviso that when n is 1 then m is 1;
	m is	an integer of 0 or 1;
	r is	an integer of 1 or 2;
10	R is	an integer of 0, 1, 2 or 3; hydrogen, C ₁ -C ₁₀ alkyl, C ₃ -C ₆ alkenyl, C ₃ -C ₆ alkynyl, C ₃ -C ₆ cycloalkyl or C ₁ -C ₁₀ alkoxy;
	R ₁ is	hydrogen or C ₁ -C ₁₀ alkyl;
	A is	C(O)X ₁ , C(S)OR ₂ , CR ₃ (OR ₄) ₂ or cyano;
	X ₁ is	OR ₅ , R ₆ , NR ₇ R ₈ or SR ₉ ;
15	R ₂ , R ₅ and R ₉ are	each independently hydrogen, C ₃ -C ₁₀ alkenyl, C ₃ -C ₁₀ alkynyl, furfuryl, C ₁ -C ₁₀ alkyl optionally substituted with one or more halogen atoms, or an alkali metal, alkaline earth metal, manganese, copper, zinc, cobalt, silver, nickel, ammonium or organic ammonium cation;
	R ₃ and R ₆ are	each independently hydrogen or C ₁ -C ₁₀ alkyl optionally substituted with one or more halogen atoms;
20	R ₇ and R ₈	are each independently hydrogen, C ₃ -C ₁₀ alkenyl or C ₁ -C ₁₀ alkyl;
	R ₄ is	C ₃ -C ₁₀ alkenyl, C ₃ -C ₁₀ alkynyl or C ₁ -C ₁₀ alkyl and when taken together R ₄ and a second R ₄ may form a ring in which R ₄ R ₄ are represented by -(CH ₂) ₂ - or -(CH ₂) ₃ -; and
25		the optical isomers thereof.

2. The method according to claim 1 wherein the safener compound is selected from the group consisting of
 - the diammonium salt of 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-6-[(2-chloro- $\alpha,\alpha,\alpha,6$ -tetrafluoro-p-tolyl)oxy]-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-3,4-dihydro-6-methoxy-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-8-chloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-6,8-dichloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-6,7-dichloro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-6-fluoro-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 7-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 6-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 8-bromo-4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-6,8-dibromo-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 4-carboxy-6,8-dimethyl-3,4-dihydro-2H-1-benzopyran-4-acetic acid;
 - 2,2',3,3',4',5'-hexahydrospiro[2H-1-benzopyran-4,3'-(2'H)-furan]-2',5'-dione;
 - 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzopyran-4-acetate, diethyl ester;
 - 45 4-carboxy-6-fluoro-3,4-dihydro-2-methyl-2H-1-benzopyran-4-acetic acid as mixture of diastereomers;
 - 4-carboxy-6-chloro-3,4-dihydro-2H-1-benzothiopyran-4-acetic acid;
 - 4-carboxy-3,4-dihydro-2H-1-benzothiopyran-4-acetic acid; and
 - 1-carboxy-1,2,3,4-tetrahydro-1-naphthaleneacetic acid.
- 50 3. The method according to claim 1 wherein the herbicide is selected from the group consisting of an imidazolinone compound, a sulfonylurea compound, a sulfamoylurea compound, an oxime compound, a 2-(4-aryloxyphenoxy)propionic acid compound, a thiocarbamate compound, a 2-chloroacetanilide compound, a dinitroaniline compound and an isoxazolyl-2-imidazolidinone compound.
- 55 4. The method according to claim 3 wherein the imidazolinone compound is selected from the group consisting of
 - 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid;

- 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinolinecarboxylic acid;
 isopropylammonium 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
 methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate;
 mixture of methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluate and methyl 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluate; and
 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-5-methylnicotinic acid.
5. The method according to claim 3 wherein the herbicide is a sulfonylurea compound selected from the group consisting of
 10 methyl O-{[3-[4,6-bis(difluoromethoxy)-2-pyrimidinyl]ureido]sulfonyl}benzoate;
 1-[*(o*-chlorophenyl)sulfonyl]-3-(4-methoxy-6-methyl-s-triazin-2-yl)urea;
 methyl O-{[[3-(4,6-dimethoxy-2-pyrimidinyl)ureido]sulfonyl}methyl}benzoate;
 methyl O-{[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-ureido]sulfonyl}benzoate;
 1-(4,6-dimethoxy-2-pyrimidinyl)-3-[3-(dimethylcarbamoyl)-2-pyridyl]sulfonylurea;
 15 ethyl 5-{[3-(4,6-dimethoxy-2-pyrimidinyl)ureido]sulfonyl}-1-methylpyrazole-4-carboxylate;
 methyl 3-{[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-ureido]sulfonyl}-2-thiophenecarboxylate;
 1-[*(o*-(3-chloropropoxy)phenyl)sulfonyl]-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea and
 ethyl o-{[(4-chloro-6-methoxy-2-pyrimidinyl)carbamoyl]sulfamoyl}benzoate.
- 20 6. The method according to claim 3 wherein the herbicide is a sulfamoylurea compound selected from the group consisting of
 1-[*(o*-(cyclopropylcarbonyl)phenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea;
 1-[*(o*-acetylphenyl)sulfonyl]-3-(4-methoxy-6-methyl-2-pyrimidinyl)urea; and
 1-[*(o*-acetylphenyl)sulfamoyl]-3-(4,6-dimethoxy-2-pyrimidinyl)urea.
- 25 7. The method according to claim 3 wherein the herbicide is an oxime compound selected from the group consisting of
 2-(O-ethyloxime) 2-butyryl-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one;
 sodium salt of methyl 5-butyryl-2,2-dimethyl-4,6-dioxocyclohexanecarboxylate 5-(O-allyloxime);
 30 2-[O-(3-chloroallyl)oxime of 5-[2-(ethylthio)propyl]-3-hydroxy-2-propionyl-2-cyclohexen-1-one;
 2-(O-ethyloxime) of 2-butyryl-3-hydroxy-5-(tetrahydro-2H-thiopyran-3-yl)-2-cyclohexen-1-one; and
 2-(O-ethyloxime) of 3-hydroxy-2-propionyl-5-(2,4,6-trimethylphenyl)-2-cyclohexen-1-one.
- 35 8. The method according to claim 3 wherein the herbicide is a 2-(4-aryloxyphenoxy)propionic acid compound selected from the group consisting of
 methyl 2-{p-[3-chloro-5-(trifluoromethyl)-2-pyridyl]-oxy}phenoxy}propionate;
 methyl 2-{p-(2,4-dichlorophenoxy)phenoxy}propionate;
 butyl 2-{p-[5-(trifluoromethyl)-2-pyridyl]oxy}phenoxy}propionate;
 butyl 2-{p-[5-(trifluoromethyl)-2-pyridyl]oxy}phenoxy}propionate, (R)-;
 40 2-ethoxyethyl 2-{p-[3-chloro-5-(trifluoromethyl)-2-pyridyl]oxy}phenoxy}propionate;
 1-{2-{p-[3,5-dichloro-2-pyridyl]oxy}phenoxy}propionyl]isoxazolidine;
 2-{(isopropylideneamino)oxy}ethyl 2-{p-[6-chloro-2-quinoxaliny]oxy}phenoxy}propionate, (R)-;
 ethyl 2-{p-[6-chloro-2-quinoxaliny]oxy}phenoxy}propionate;
 ethyl 2-{p-[6-chloro-2-benzoxazolyl]oxy}phenoxy}propionate;
 45 N-benzoyl-N-(3,4-dichlorophenyl)alanine, ethyl ester;
 2-{(2,4-dichloro-m-tolyl)oxy}-2-methylpropionanilide;
 ethyl 2-{p-[6-chloro-2-benzoxazolyl]oxy}phenoxypropionate;
 ethyl 2-{p-[6-chloro-2-benzothiazolyl]oxy}phenoxy}propionate;
 N-benzoyl-N-(3-chloro-4-fluorophenyl)alanine, isopropyl ester;
 50 N-benzoyl-N-(3-chloro-4-fluorophenyl)alanine, methyl ester; and
 methyl p, α -dichlorohydrocinnamate.
9. The method according to claim 3 wherein the herbicide is a thiocarbamate compound selected from the group consisting of
 55 ethyl dipropylthiolcarbamate;
 S-ethyl diisobutylthiocarbamate;
 S-propyl dipropylthiocarbamate;
 S-ethyl hexahydro-1H-azepine-1-carbothioate;

S-(*p*-chlorobenzyl) diethylthiocarbamate; and
 S-benzyl bis(1-methylpropyl)thiocarbamate.

10. The method according to claim 3 wherein the herbicide is a 2-chloroacetanilide compound selected
 5 from the group consisting of
 2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-o-acetotoluidide;
 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide;
 N-(butoxymethyl)-2-chloro-2'-ethylacetanilide;
 10 2-chloro-2',6'-diethyl-N-(2-propoxyethyl)acetanilide; and
 2-chloro-N-isopropylacetanilide.
11. The method according to claim 3 wherein the herbicide is a dinitroaniline compound selected from the
 group consisting of
 15 N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine;
 α,α,α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine;
 3,5-dinitro-N⁴,N⁴-dipropylsulfanilamide;
 N-butyl-N-ethyl- α,α,α -trifluoro-2,6-dinitro-p-toluidine;
 20 2,6-dinitro-N,N-dipropylcumidine; and
 N-ethyl- α,α,α -trifluoro-N-(2-methylallyl)-2,6-dinitro-p-toluidine.
12. The method according to claim 3 wherein the herbicide is an isoxazolyl-2-imidazolidinone compound
 selected from the group consisting of
 25 3-(5-tert-butyl-3-isoxazolyl)-4-hydroxy-1-methyl-2-imidazolidinone; and
 3-(5-tert-butyl-3-isoxazolyl)-1-methyl-2-oxo-4-imidazolidinyl methyl carbamate.
13. A safened herbicidal composition which is characterized by a herbicidally effective amount of a
 30 herbicide and an effective antidotal amount of a safener compound having the structural formula



- 40 wherein
- X is O, S(O)_q or CH₂;
- q is an integer of 0, 1 or 2;
- Z, Z₁ and Z₂ are each independently hydrogen, halogen, C₃-C₁₀ alkenyl, C₃-C₁₀ alkynyl, furfuryl, C₁-C₇ alkoxy, C₃-C₁₀ alkenyloxy, Z₃C(O), Z₃S(O)_p,
- 45 C₁-C₁₀ alkyl optionally substituted with one or more halogen atoms, hydroxy groups, amino groups, thio groups, C₁-C₅ alkylcarbonyl groups or C₁-C₅ alkoxy groups, or
- 50 phenoxy optionally substituted with one or more halogen atoms or C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms;
- Z₃ is C₁-C₆ alkyl;
- Z₄ is C₁-C₆ alkyl;
- p is an integer of 0, 1 or 2;
- 55 Y and Y₁ are each independently hydrogen, C₁-C₆ alkyl, halogen, phenyl, C₁-C₆ alkoxy, amino or C₁-C₆ alkylcarbonyl; --- represents a single or double bond with the proviso that when --- represents a double bond then Y₂ is not present;

	W and W ₁ are	each independently (CRR ₁) _n A, and when taken together with the carbon atom to which they are attached W and W ₁ may form a ring in which WW ₁ is represented by the structure:
5		-(CH ₂) _m C(O)OC(O)(CH ₂) _n -
	n is	with the proviso that when n is 1 then m is 1;
	m is	an integer of 0 or 1;
10	r is	an integer of 1 or 2;
	R is	an integer of 0, 1, 2 or 3;
	R ₁ is	hydrogen, C ₁ -C ₁₀ alkyl, C ₃ -C ₆ alkenyl, C ₃ -C ₆ alkynyl, C ₃ -C ₆ cycloalkyl or C ₁ -C ₁₀ alkoxy;
15	A is	hydrogen or C ₁ -C ₁₀ alkyl;
	X ₁ is	C(O)X ₁ , C(S)OR ₂ , CR ₃ (OR ₄) ₂ or cyano;
	R ₂ , R ₅ and R ₉ are	OR ₅ , R ₆ , NR ₇ R ₈ or SR ₉ ;
	R ₃ and R ₆	each independently hydrogen, C ₃ -C ₁₀ alkenyl, C ₃ -C ₁₀ alkynyl, furfuryl, C ₁ -C ₁₀ alkyl optionally substituted with one or more halogen atoms, or an alkali metal, alkaline earth metal, manganese, copper, zinc, cobalt, silver, nickel, ammonium or organic ammonium cation;
20	R ₇ and R ₈	are each independently hydrogen or C ₁ -C ₁₀ alkyl optionally substituted with one or more halogen atoms;
	R ₄ is	are each independently hydrogen, C ₃ -C ₁₀ alkenyl or C ₁ -C ₁₀ alkyl; C ₃ -C ₁₀ alkenyl, C ₃ -C ₁₀ alkynyl or C ₁ -C ₁₀ alkyl and when taken together R ₄ and a second R ₄ may form a ring in which R ₄ R ₄ are represented by -(CH ₂) ₂ - or -(CH ₂) ₃ -; and
25		the optical isomers thereof.

14. The composition according to claim 13 wherein the herbicide is selected from the group consisting of an imidazolinone compound, a sulfonylurea compound, a sulfamoylurea compound, an oxime compound, a 2-(4-aryloxyphenoxy)propionic acid compound, a thiocarbamate compound, a 2-chloroacetanilide compound, a dinitroaniline compound and an isoxazolyl-2-imidazolidinone compound.

15. A compound having the structural formula

35		
40		
45	wherein	
	X is	O or S(O) _q ;
	q is	an integer of 0, 1 or 2;
	Z, Z ₁ and Z ₂ are	each independently hydrogen, F, Cl, Br, C ₁ -C ₄ alkoxy, phenoxy optionally substituted with one or more halogen atoms or C ₁ -C ₄ alkyl groups optionally substituted with one or more halogen atoms, or C ₁ -C ₄ alkyl optionally substituted with one or more halogen atoms, C ₁ -C ₄ alkoxy groups or hydroxy groups,
50		provided that only one of Z-Z ₂ is C ₁ -C ₃ alkoxyalkyl or phenoxy optionally substituted with one or more halogen atoms or C ₁ -C ₄ alkyl groups optionally substituted with one or more halogen atoms;
55	Y and Y ₁ are	each independently hydrogen, F, Cl or C ₁ -C ₃ alkyl, provided that when Y is F or Cl, then Y ₁ is hydrogen;

W is CH_2A or when taken together with W_1 , WW_1 is represented by the structure
- $\text{CH}_2\text{C}(\text{O})\text{OC}(\text{O})-$;
 W_1 is A or when taken together with W, W_1W is represented by the structure - $\text{C}(\text{O})$ -
 $\text{OC}(\text{O})\text{CH}_2-$;
5 A is $\text{C}(\text{O})\text{X}_1$ or $\text{CH}(\text{OR}_4)_2$;
 X_1 is OR_5 or SR_9 ;
 R_5 is hydrogen, $\text{C}_1\text{-}\text{C}_6$ alkyl, $\text{C}_3\text{-}\text{C}_6$ alkenyl, $\text{C}_3\text{-}\text{C}_6$ alkynyl or
an alkali metal, alkaline earth metal, manganese, copper, zinc, cobalt, silver,
nickel, ammonium or organic ammonium cation;
10 R_9 is hydrogen, $\text{C}_1\text{-}\text{C}_6$ alkyl, $\text{C}_3\text{-}\text{C}_6$ alkenyl or $\text{C}_3\text{-}\text{C}_6$ alkynyl;
 R_4 is $\text{C}_1\text{-}\text{C}_6$ alkyl and when taken together R_4 and a second R_4 may form a ring in
which R_4R_4 are represented by -(CH_2)₂- or -(CH_2)₃-; and
the optical isomers thereof;
provided that when Y is hydrogen and Y_1 is hydrogen or $\text{C}_1\text{-}\text{C}_3$ alkyl, then one of Z, Z_1 or Z_2 is
15 phenoxy optionally substituted with one or more halogen atoms or $\text{C}_1\text{-}\text{C}_4$ alkyl groups optionally
substituted with one or more halogen atoms.

16. The compound according to claim 15

4-carboxy-6-[(2-chloro- $\alpha,\alpha,\alpha,6$ -tetrafluoro-p-tolyl)oxy]-3,4-dihydro-2H-1-benzopyran-4-acetic acid.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 94 10 2568

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)						
A	EP-A-0 012 158 (CIBA-GEIGY AG) ---		A01N25/32 C07D311/58 C07D335/06 C07D493/10 //(C07D493/10, 311:00,307:00)						
A	EP-A-0 065 392 (IMPERIAL CHEMICAL INDUSTRIES PLC.) ---								
A	J. MED. CHEM., 34(3), 1011-18 1991 Mylari, Banavara L. et al 'A highly specific aldose reductase inhibitor, ethyl 1-benzyl-3-hydroxy-2(5H)-oxopyrrole-4-carboxylate and its congeners' ---								
A	J. HETEROCYCL. CHEM., 8(1), 155-6 1971 Rice, Leonard M. et al 'Spirans. XVII. Spirans derived from 4-chromanone' -----								
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)						
			A01N C07D						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>8 June 1994</td> <td>Donovan, T</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	8 June 1994	Donovan, T
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